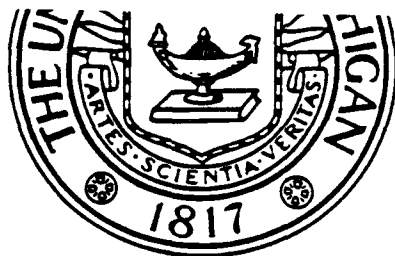




# Final Report:

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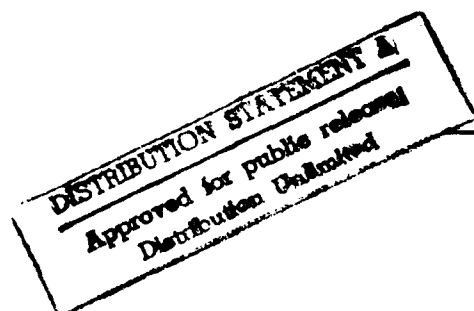


## *Workshop on Surface Science and Technology*

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AUG 3 1992  
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*Ann Arbor, Michigan*

*November 7-9, 1990*



*Sponsored by:*

*The University of Michigan  
&  
Army Research Office*

92-20887



*Workshop Chairmen: John C. Bilello and Robert R. Reeber*

*March, 1992*

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# **Final Report**

*Submitted: March, 1992*

## **WORKSHOP ON: SURFACE SCIENCE & TECHNOLOGY**

*Sponsored by:*

*The University of Michigan*

*&*


*Army Research Office*

*November 7-9, 1990*

Surface Science and Technology  
Workshop

The objective of this workshop was to review and assess the state of the art of surface science and technology as well as to identify new research opportunities essential for the understanding and control of surface degradation, adhesion, corrosion and wear. A cross-section of Academic, Army and NASA professionals contributed their talents. It is anticipated that the knowledge gained through programs focussing on the Army and national needs will result in new materials coating systems that have novel properties, increased durability and reliability and the potential for significantly lowering the Army's maintenance and logistics costs.

The enthusiasm of the participants as well as the ideas generated in this important area indicates that the workshop was a timely one with many potential benefits possible from future research investments.

  
ROBERT R. REEBER  
Army Research Office

  
JOHN C. BILELLO  
University of Michigan

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## EXECUTIVE SUMMARY

The workshop was a review and assessment of research, research needs and future opportunities for the general area of surface science and technology, these topics were previously discussed in detail in December 1982 at the ARO Protective Coatings Workshop. Notable changes in emphasis during the past ten years can be summarized as follows:

- \* There has been a major shift away from electroplating research to research that mitigates environmental problems of electroplating and other solution coating processes.

- \* Ion beam and laser modification methods both singly and in tandem (Beam technologies) offer significant promise as environmentally attractive surface treatments especially for refractory ceramics and for reduction of friction and wear. Molecular beam Epitaxy and Sputtering also show promise of applications beyond electronic component technology. These methods although amenable to quality manufacturing require development and installation of capital intensive equipment.

- \* Novel laser, positron, ion and electron spectroscopies as well as the availability of larger scale more intense synchrotron induced radiation has expanded the sensitivity and capability of surface characterization.

- \* Tribological research especially for ceramics for heat engine applications, tribochemistry of surfaces, corrosion protection of composites, and coatings by design for specific applications have become increasingly more important.

- \* Novel Non-destructive evaluation (NDE) of coatings to estimate remaining life or provide warnings of impending failure and other smart coatings that provide stealth functions are within the realm of possibility.

- \* Theoretical models relating coating processes to performance can suggest specific new experiments to confirm their validity. In general it is important that real-time in-situ studies at the nanolevel be made on real systems, understanding meanwhile that studies on model systems are also valuable.

- \* Continued efforts should be made to formalize technology transfer between the different Army research and development (techbase) organizations. Achievements from Army laboratory investments in related applied academic research will lead to increased faculty interest in Army problems.

- \* Specific recommendations relevant to coating characterization, electroplating and surface treatments, tribology, conversion coatings, and coatings by design are given in the specific panel reports that follow.

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## Report of Research Needs For Coating Characterization

Henry W. White, Panel Chair  
Department of Physics and Astronomy  
University of Missouri  
Columbia, MO 65211

Panel members: John Bilello, University of Michigan; William Miller, University of Missouri; Albert Schultz, Ionwerks; Jag Singh, NASA-Langley; Ig Tsong, Arizona State University; John Weare, University of California-San Diego; William Winfree, NASA-Langley.

Basic research involving real-time in-situ analysis of nano-chemistry, bonding, nucleation, growth, as well as property characterization at the atomic and molecular level when correlated with coating requirements can provide the information necessary for new theoretical approaches to coating technology.

Specific concerns and recommendations are as follows:

- There exists a need to develop real-time, in-situ techniques that can be used to monitor the growth of a range of coatings. Great strides could be made by coupling characterization with growth. It would improve coatings and provide an ability to tailor coatings to desired features and specifications.

- We need a better understanding of growth and protection mechanisms at the atomic and molecular level. Ongoing theoretical support is necessary.

- It is important that studies be made on real systems, understanding meanwhile that studies on model system are also valuable.

- Various types of information on coatings are required to understand their nucleation and growth in relation to their physical and mechanical properties. These include structure, energy transfer, electronic and vibrational properties, ion movement, microstructure (and how it relates to macrostructure), surface and interface roughness, and subsurface structure.

- A cross-coupling of various characterization techniques gives real power to obtain critically important information. As an example, relating interfacial dislocations observed by STM to bulk strain measured by x-rays.

- The ability to determine phase distributions in real-time during coating growth would be especially powerful. Techniques with promise include (synchrotron) x-rays, RHEED, Raman and ion scattering.

- Many of the advanced techniques for characterization are now affordable, either on-site or at a national facilities. These facilities and techniques include synchrotrons, reactors, accelerators, Auger, XPS, etc.

- Many advanced techniques are complementary, for example x-ray, neutron, electron, and ion scattering.

- Several of these characterization techniques are non-destructive and are sufficiently low cost and operationally simple that they can be used for growth analyses in a production environment. These include photoacoustic/photothermal and thermal imaging.

- Techniques are needed that will give atomic and molecular species with high spatial resolution.

- It is important to know the function of a coating. Such information is necessary to know how to best characterize the coating and how to best approach funding sources to obtain necessary support for improving and understanding protective coatings.

It is informative to know the salient features for each technique, such as probe area and depth, spatial resolution, and special sensitivity. Features for several representative techniques are listed below.

#### Scanning Tunneling Microscopy (STM):

Application:	surface structure
Spatial Resolution:	0.1 nm
Depth Probed:	first surface layer
Elemental Sensitivity:	N.A.
Maximum Area:	10 microns x 10 microns
Depth Resolution:	surface layer
Comments:	Non-destructive technique with atomic resolution on conducting surfaces.

#### Atomic Force Spectroscopy (AFM):

Comments: Another probe microscopy which yields surface images similar to those of STM. Images can be obtained on insulating surfaces. Sensing phenomena can be based on tunneling current, light deflection, etc.

#### Direct Recoil Spectroscopy (DRS):



### Low Energy Ion Scattering (LEIS):

### Secondary Ion Mass Spectroscopy (SIMS):

Application: surface structure and elemental composition  
Spatial Resolution: 200 microns  
Depth Probed: 2-3 monolayers; depth profiling possible  
Elemental Sensitivity: 1 amu through mass 28 amu (DRS)  
Comments: Combined pulsed time-of-flight techniques, non-destructive with  $10^{10}$  ions/cm<sup>2</sup> sensitivity, capable of giving in situ and real time stoichiometry on surface during film growth. DRS and LEIS can be done up to 1 torr pressure.

### Thermal Imaging:

Application: surface structure  
Depth Probed: several mm  
Elemental Sensitivity: N.A.  
Maximum Area: up to 100 cm<sup>2</sup>  
Depth Resolution: 1 micron  
Comments: Non-destructive technique, can detect variations in ion implantation, delaminations, cracks, and coating thickness. Inexpensive, no special surface preparation.

### Raman Spectroscopy:

Application: Identification of molecular species, compounds and structure  
Spatial Resolution: 1 micron (with microRaman)  
Depth Probed: varies with sample  
Elemental Sensitivity: N.A.  
Maximum Area: cm<sup>2</sup>  
Depth Resolution: several microns, given special aperturing

### LEED/RHEED:

Application: Non-destructive analysis of surface crystallography including lattice parameters identification of adsorbed species.  
Spatial Resolution: 0.1 - 1.5 nm (nanometers)  
Depth Probed: can be deduced from IV characteristics  
Elemental Sensitivity: virtually all  
Maximum Area: cmx cm  
Depth Resolution: 0.05Å°  
Comments: Non-destructive, can be used in situ in growth chambers.

### Infrared Spectroscopy:

Application: Identification of molecular species, compounds  
Spatial Resolution: 1 micron (with microIR)  
Depth Probed: varies with sample  
Elemental Sensitivity: N.A.  
Maximum Area: cm<sup>2</sup>  
Depth Resolution: several micron, given special aperturing

### Neutron Diffraction (Elastic):

Application: crystal and thin film structure  
Spatial Resolution: mm  
Depth Probed: entire sample  
Elemental Sensitivity: deduced from analysis of diffraction profile  
Maximum Area: cm x cm  
Depth Resolution: N.A.  
Comments: Powder diffraction techniques are now quite advanced, also.

### Grazing Incidence Neutron Diffraction:

#### Grazing Incidence X-ray Diffraction:

Application: Surface and interface microchemistry and microstructure  
Spatial Resolution: mm x mm  
Depth Probed: mm  
Elemental Sensitivity: neutrons and x-rays very complementary  
Maximum Area: cm x cm  
Depth Resolution: nm  
Comments: Non-destructive technique for thin films with depth profiling possible.

### Neutron Energy Loss Spectroscopy:

Application: Hydrogen detection in metals at low concentrations  
Spatial Resolution: mm x mm  
Depth Probed: cm  
Elemental Sensitivity: hydrogen specifically  
Maximum Area: cm x cm  
Depth Resolution: N.A.  
Comments: Non-destructive technique for analysis of hydrogen in metals at concentrations down to 10 weight ppm, or lower.

### Positron Lifetime Spectroscopy:

Application: Distribution of sizes and shapes of  
microvoids, free volume pores.

Spatial Resolution: mm x mm

Depth Probed: 0.01 to several mm

Elemental Sensitivity: N.A.

Maximum Area: cm x cm

Depth Resolution: N.A.

Comments: Non-destructive technique for analysis of films from  
0.01 to several mm thickness.

## Report of Electroplating and Waste Treatment Panel

Joseph A. Walden  
Physical Science Branch  
Benet Laboratories  
Watervliet, New York

Panel Members: John Dash, Portland State; Geoff Prentice, Johns Hopkins University; Rolf Weil, Stevens Institute of Technology; C.A. Ross, Harvard University; Ronald Jackson, U.S. Army Toxic & Hazardous Materials Agency; George MacAlister, TACOM; and Jim Waber, Michigan Technological University.

### Summary

The members of the panel discussed issues of future research pertinent to electroplating and waste treatment. After extensive and vigorous discussion, the following recommendations were made:

a. Fundamental research should be conducted to identify solvent/solute systems which would enable the deposition of metals such as chromium without the accompanying hydrogen embrittlement. Dimethyl formamide was suggested to be such a solvent.

b. Basic research should be supported in the area of electrodeposition of chromium metal from chromium (III)-based baths. Presently, the technology is limited by the inability to plate Cr(0) from such baths at thicknesses .002 in. The ability to deposit 0.010 in. thickness chromium metal should be a goal of such a project. Present chromium (VI) baths are much more hazardous than chromium (III) baths, thus giving impetus to the above suggested project requirements in that pollution abatement can be realized.

c. Chromium (VI) reclaim techniques should be investigated to enable loop-closing in industrial electrodeposition systems.

d. Various instrumental methods for coating evaluation were discussed and include:

(1) Positron annihilation studies to investigate the porosities of metallic and non-metallic coatings.

(2) Force and scanning tunneling microscopy studies to elucidate mechanisms of electrodeposition of individual atom layers.

e. Hardware and software are available to enable molecular orbital calculations on transition metal ions (especially chromium). It was suggested that such a system be utilized to investigate fundamental mechanisms of electrodeposition.

f. Fundamental studies on the mechanical properties of electrodeposits should be performed. Application of thin film characterization techniques would permit detailed correlation of these mechanical measurements to the microstructure and chemistry of the electrodeposits. Since much of this equipment is already in place, an opportunity for leveraging of resources is available.

g. With respect to fasteners (bolts particularly) there should be fundamental studies for:

- (1) Increasing corrosion protection
- (2) Decreasing coefficient of friction
- (3) Reducing hydrogen embrittlement

h. There are dragout problems encountered in the treatment of industrial sludge which results from electrodeposition processes. New metal reclamation techniques for sludges containing many kinds of metal ions should be investigated.

i. Fundamental studies of the "bath-poisoning" phenomenon should be considered. This would represent an area where significant cost savings could be realized.

j. Fatigue of electronic components undergoing low-frequency thermal cycling, especially if composed of several materials having different expansion coefficients, is responsible for degradation of system performance. Studies of the fatigue properties of such composites should be initiated.

k. Adhesion studies of deposits on non-metallic substrates should be considered.

l. Studies of processing of composites for better corrosion and wear resistance should be encouraged.

m. Stress studies of deposits should be conducted because of the effect of stress on corrosion and adhesion.

n. Investigations of the electrodeposition of semi-conductors and dielectrics should be performed.

In conclusion, the very extensive list of suggestions for future research reveals that there are many opportunities for fundamental scientific studies in the areas of electroplating and wastewater treatment.

## Report for Research Needs on Tribology

James W. Mayer, Panel Chair  
Dept. of Materials Science and Engineering  
Cornell University

Panel Members: Traugott Fischer, Stevens Institute of Technology; Richard Burns, University of Illinois, Chicago; Tom Jervis, Los Alamos National Laboratory; Robert Kusy, University of North Carolina-CH; William Lanford, SUNY-Albany, Lawrence Mizerka, Army Materials Technology Laboratory.

The recommendations for future actions of this committee are divided into technical recommendations, i.e. areas of research which are recommended for emphasis and support, and recommendation for technology transfer and integrations; the latter are actions which the committee feels would increase the effectiveness of the research being supported now and in the future.

### Summary

The research programs supported by ARO have demonstrated that surface modification of metals by ion beams or laser lead to improved tribological performance with reduced friction and wear. Technology transfer to applied areas is recommended. Ceramics represent the next frontier for materials applications in engines. Surface processing by ion beams and lasers does strengthen the ceramics; however, the basic mechanisms of surface chemistry, wear, and modification are not well understood. In area of ceramics we recommend continued support of basic research on surface modification. We also recommend exploratory programs in the chemistry of wear and lubrication of ceramics (tribochemistry).

### A. TECHNICAL RECOMMENDATIONS:

#### 1. Surface Modification

In the ARO Program it has been demonstrated that the tribological properties of metals can be greatly improved by the use of ion beam modification of metal surfaces. This ion implantation technology has been applied successfully at the Army Helicopter Depot in Corpus Christi Texas. We recommend continued emphasis on technology transfer in areas where improved wear and friction properties are important in the Army mission. The situation is different in the case of ceramics where improvement in tribological performance has been shown in research studies but not under field conditions. Surface processing using both laser and ion beams has been demonstrated to increase the strength of ceramic components. Further research to demonstrate both the tribological and structural benefits of beam processing

should be pursued. Combination techniques involving both laser processing and ion implantation are especially promising.

## 2. High Temperature Tribology

High-Temperature lubricants are needed for TACOM as well as for novel engine developments using ceramic and metal technology. The behavior of liquid high-temperature lubricants must be studied from a scientific viewpoint to accelerate development of high-performance lubricants. Of interest are the temperature-dependent rheology of the liquids, but more importantly the tribochemical interactions between lubricant and solid.

The high-temperature tribological properties of some ceramics are being studied in several laboratories. These studies are now restricted to unlubricated sliding. This work is still too empirical, limited to reporting wear rates. A more scientific understanding is necessary: role of temperature dependence of relevant mechanical properties, chemical and tribochemical reactions with the environment or lubricant, surface segregation as they influence friction and wear.

## 3. Ceramics

Much progress has been made in the tribology of ceramics in the past five years and research is very active. However, more work is required in two areas:

**Tribochemistry of Ceramics:** Lubricant components (additives) are needed to improve the tribological performance of ceramics. The wear inhibitors and other additives presently in use are adapted to the chemistry of iron, they are not effective for ceramics. Humidity plays an excessive role in present applications. A scientific and interdisciplinary study of the tribochemistry of chemistry is recommended. Tribologists must work with inorganic chemists and with geologists who have accumulated a large amount of knowledge on these materials.

**Surface Mechanics of Ceramics:** The contact mechanics is not well described at this time. Experimental observations have been made that are incompatible with present theories of surface contact mechanics. This is important for service in the mixed lubrication regime where surface topography is determinant; it is also important for an understanding of the techniques and requirements of running in.

#### 4. Surface Technology

Coatings are presently used in development of high temperature engines and other designs for severe service rather than bulk ceramics that are expensive to machine and often subject to fracture. Active programs exist in ARO, but we recommend (see A above) more integration with the characterization and performance evaluation programs.

#### 5. Reactive Technology (or The Dynamic Surface)

It is possible to develop materials, especially in extreme service that do not necessarily avoid reaction with the environment but use it to improve performance. Research in the chemistry and properties of materials that become better in service. (Alumina cutting tools forming surface perovskites are an example, stainless steels for corrosion resistance are another; this concept could be generalized).

#### 6. Theory of Friction

Early work is appearing exploring the fundamental (microscopic) phenomena of energy dissipation in terms of phonon generation. By molecular dynamics with well calculated cohesion, by modeling of liquid behavior in boundary lubrication and rudimentary modeling of tribochemical reactions. This is a level of scientific sophistication not before used. Progress in this area must be considered as an important possible source of innovation.

### B. TECHNOLOGY TRANSFER AND INTEGRATION

This committee felt that the present ARO program constitutes a very good "portfolio" of research: the important elements for the technology serving the Army are in place. A greater integration of these parts into a coherent body of knowledge would greatly increase the power and usefulness of the work. In addition, the individual research programs could benefit from a degree of collaboration between principal investigators working in related but different areas.

1. It is recommended that the technology transfer between the different Army research and development (techbase) organizations (6.1 through 6.3) be strengthened and where appropriate formalized.

Information from 6.1 through 6.3 on results and efforts should be augmented to integrate them into technology and systems. Information should be transferred from 6.3 and 6.2 (applied research) to 6.1 (basic research) about the needs



that can be addressed by fundamental research. Workshops, and small group meetings offer an important vehicle for increasing the impact of this and related research on Army technology.

The total package of results could then be more easily transmitted to 6.2 and 6.3. Achievements from Army laboratory investments in related applied academic research will lead to increased faculty interest in Army problems.

## Report on Research Needs for Conversion Coatings

Florian Mansfeld, Panel Chair  
Department of Materials Science and Engineering  
University of Southern California  
University Park, Los Angeles, CA 90089-0241

Panel Members: George MacAllister, TACOM; Dale Barkey, University of New Hampshire; G. R. Lakshminarayanan, ARDEC; Toshi Sugama, Brookhaven National Laboratory.

### Summary

Conversion coatings have several important applications related to vehicles, armor, personal weaponry and ground installations. They need to have good adhesion and pass the standard tests which are required by military and other specifications. Field applications may require color modifications of the original surface coatings. Environmental concerns with current chromate coatings and chromium plating has created needs for alternate coating processes. Future directions toward all polymer composite hulls and helicopters have introduced requirements for polymer composite coatings. In addition to environmental and radiation (solar) stability these need to be resistant to hazardous threats and decontamination solutions.

The following research areas highlighted below show promise:

- \* Polymer modified phosphate conversion coatings show promise as the morphology can be tailored for specific applications.

- \* Further research is needed on organo-metallic coatings based upon pre-ceramic polymer/sol-gel and other precursors so that they are suitable for a range of reactive environments. These have potential high temperature applications.

- \* Fundamental characterization of empirically derived processes and coatings often gives insights leading to improved function.

- \* Replacements for chromate conversion coatings for aluminum and magnesium are being driven by environmental concerns. Ce-Mo and several other conversion coatings which are porous provide an excellent base for application of a sealant, primer and topcoats. These could have important engineering applications.

\* Research on passivating interfaces, thermal expansion mismatch, porous conversion coatings, conductive polymer coatings, versatile polymer composite coatings, self-healing coatings. A useful approach for specific coating requirements must consider base material-conversion coat and topcoat interactions as the system relates to the operating environment.

\* Significant understanding can be obtained by theoretical modeling of chemical interactions, bonding as they relate to the mechanical/environmental stability of specific coatings.

\* Tech transfer of coatings research is expedited by data from standard tests (salt spray, cyclic humidity temperature, and resistance to specific pollutants).

Report on Surface Coatings  
By Design

William A. Goddard III, Panel Chair<sup>+</sup>  
Laboratory for Chemical Physics  
California Institute of Technology  
Pasadena, California 94720

Panel Members: Richard Brown, Univ. of Rhode Island; Robert Reeber, ARO; John Weare, Univ. California, LaJolla; Alfred Smith, William Upchurch, NASA-Langley, Hampton VA.

Summary

There was general agreement of a need for greater understanding of the fundamentals of theory and experiment both on the micro and macro scale. Because of the complexity of coatings, and their interactions with a wide range of service environments, a number of approaches that offer aid to understanding and design need to be considered. These include such things as quantum chemistry, molecular dynamics, statistical physics, finite element analysis, crystal nucleation, growth and morphology etc. Service conditions such as thermal expansion mismatch, residual and thermal stresses levels, can be simulated if thermal expansion and elastic constants are known. A realm of techniques exist to simulate properties at various levels from the atomic to the microscopic. These when incorporated into an overall model can suggest key well characterized experiments that verify the overall model validity.

In the short term it is important to carefully characterize good coatings that have been developed empirically. Because coatings are complex, starting from scratch to design a superior one is extremely difficult and probably not cost-effective.

\* Improved coatings by design will require advances in fundamental science of an interdisciplinary nature. This will involve physics, chemistry, materials science, mechanical engineering and large scale computational science.

\* Theoretical models relating coating processes to performance can suggest specific new experiments that confirm their validity. Studies are needed to understand design principles and how these relate to application requirements.

\* In-situ characterization to follow film/coating formation of "good" systems is important. Signatures can be correlated with processing steps and subsequently related to the performance of improved coatings.

\* Smart coatings with imbedded sensors can be developed which warn of impending failure (spot failure through color indication for instance). As mechanisms are better understood it may become possible to develop molecular level sensors. For instance a heavy ion can tag a degradation mode or in some other way sensitize local degradative effects. A variety of external probes (light, heat, alpha rays etc.) could then be utilized non-destructively as an NDE or metrological device.

\* A range of coating properties must be considered including such things as crack propagation across thin coatings and interfaces, frictional relationships with and without lubricants, and degradative modes of various types.

+ Conference chairmens' summary edited from video tape.

# WORKSHOP PROGRAM

## **SURFACE SCIENCE AND TECHNOLOGY**

Sponsored by: *The University of Michigan - Army Research Office*  
Webers Inn, Ann Arbor, Michigan

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**WEDNESDAY AFTERNOON**  
**NOVEMBER 7, 1990**

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- 1:00 p.m.      Opening Remarks—John Bilello, The University of Michigan, Co-Chair
- 1:05 p.m.      Introduction—Robert Reeber, Army Research Office, Co-Chair
- 1:25 p.m.      Overview Lecture—*First Principle Calculations of the Properties of Clusters and New Materials?*—John Weare, University of California, San Diego

**Hydrogen Characterization/Mitigation**—William Lanford, SUNY, Albany, Chair

- 2:00 p.m.      *Positron Techniques*—James Waber, Michigan Technological University
- 2:30 p.m.      *Neutron Energy Loss Spectroscopy*—Walter Meyer, Syracuse University
- 2:50 p.m.      *Surface Modification*—Richard Brown, M.T.L Watertown/Univ. of Rhode Island
- 3:10 p.m.      Question/Answer Period
- 3:30 p.m.      Coffee Break

**Electroplating and Waste Treatment Panel**—Joseph Walden, Benet Weapons Lab, Chair

John Dash, Portland State University  
Geoff Prentice, Johns Hopkins University  
Caroline Ross, Harvard University  
Ronald Jackson, U.S. Army-THAMA

- 5:00 p.m.      Dinner (no host)
- 7:00-9:00 p.m. **Surface Treatment and Coating Technology**—Poster Session

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**THURSDAY MORNING  
NOVEMBER 8, 1990**

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**Conversion Coatings/Inhibitors—William Goddard, California Inst. of Technology, Chair**

- 8:30 a.m.    *Polymer Modified Conversion Coatings*—Toshifumi Sugama, BNL
- 8:50 a.m.    *Conductive Corrosion Inhibitive Polymer Films*—Dale Barkey, University of New Hampshire
- 9:10 a.m.    *Inhibitor Characterization and Theory*—Henry White, University of Missouri, Columbia
- 9:40 a.m.    *Inhibitive Coatings on Metal-Matrix Composites*—Florian Mansfeld, University of Southern California
- 10:00 a.m.    Question/Answer Period
- 10:20 a.m.    Coffee Break

**Tribology/Solid Lubricants—J. Wayne Jones, University of Michigan, Chair**

- 10:40 a.m.    *Friction and Wear of Materials: A Review*—T. Fischer, Stevens Institute of Technology
- 11:10 a.m.    *Solid Lubricant Characterization*—Richard Burns, University of Illinois, Chicago
- 11:30 a.m.    *Laser Processing of Materials*—Thomas Jervis, LANL
- 11:50 a.m.    Question/Answer Period
- 12:10 p.m.    Lunch (Catered)

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**THURSDAY AFTERNOON  
NOVEMBER 8, 1990**

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**Ceramic Coatings/Surface Modification**—Robert Kusy, University of North Carolina, Chair

- 1:30 p.m.     *Ion-Induced Disorder in Ceramics*—James Mayer, Cornell University
- 2:05 p.m.     *Thin Film Phase Diagrams*—Carolyn Aita, University of Wisconsin, Milwaukee
- 2:25 p.m.     *Modulated Coatings*—Bernard Gallois, Stevens Institute of Technology
- 2:45 p.m.     Question/Answer Period
- 3:05 p.m.     Coffee Break

**Non-Destructive Evaluation of Coatings**—Steve Yalisove, University of Michigan, Chair

- 3:25 p.m.     *States of Stress and Long Term Reliability*—John Bilello, University of Michigan
- 3:55 p.m.     *Electron Tunneling Microscopy*—I. Tsong, Arizona State University
- 4:15 p.m.     *Compound Coating Characterization*—J. Albert Schultz, Ionwerks
- 4:35 p.m.     *Ion Beam Analysis of Surfaces*—Gary Was, University of Michigan
- 4:55 p.m.     Question/Answer Period
- 5:15 p.m.     Dinner (no host)



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**FRIDAY MORNING  
NOVEMBER 9, 1990**

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- 8:30 a.m. Charge to Panels—Robert Reeber, Army Research Office
- 8:50 a.m. Panel Meetings—John Bilello, University of Michigan, Panel Chair
1. Coating Characterization: Henry White, Chair  
University of Missouri, Columbia
  2. Electroplating and Surface Treatment: Joseph Walden, Chair  
Benet Weapons Lab
  3. Tribology: James Mayer, Co-Chair  
Cornell University  
Traugott Fischer, Co-Chair  
Stevens Institute of Technology
  4. Conversion Coatings/Inhibitors: Florian Mansfeld, Chair  
University of Southern California
  5. Surface Coatings by Design: William Goddard, Chair  
California Institute of Technology
- 10:20 a.m. Panel Summary
- 11:00 a.m. Panel Report (Subpanel Chairs)—John Bilello, University of Michigan, Panel Chair
- 12:20 p.m. Closing Remarks—Co-Chairs
- 12:30 p.m. Lunch (no host)
- 2:00 p.m. Tour of The University of Michigan, Materials Research Facilities
- 3:30 p.m. Adjournment

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## Thin Film 'Phase Diagrams'

Carolyn R. Aita

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Reactive sputter deposition is a widely-used glow discharge method for growing high melting point materials near room temperature and metastable phases and multiphase structures not attainable in bulk material grown under conditions of thermodynamic equilibrium. This talk is concerned with the importance of developing process parameter-growth environment-film property relationships for sputter deposited metal oxides. These thin film "phase diagrams" allow materials to be reproducibly grown, are a first step towards developing growth processes that can be transferred from machine-to-machine, and give fundamental insight into the growth process. Both optical and mass spectrometric methods for monitoring the sputtering discharge are discussed.

In these experiments, reactive sputter deposition was carried in a parallel-plate electrode apparatus. The metal target was placed over the cathode to which a large negative voltage was applied. The substrates, onto which the films were deposited, were placed over the anode kept near ground potential. The sputtering gas, a combination of rare and reactive gas, formed a self-sustained, low pressure ( $\sim 10^{-2}$  torr) glow discharge. Radio frequency excitation allowed the use of a nonconducting target, which can be the case when a metal target surface becomes oxidized upon being sputtered in an oxygen-bearing discharge.

Process parameters that were varied independently were nominal oxygen content in the discharge, the type of rare gas used in conjunction with oxygen, and the cathode voltage. The deposition rate and discharge power depended upon combinations of these parameters.

The relative flux of metal, metal-oxide, and oxygen species that arrive at the substrate are adsorbed and ultimately incorporated into stable nuclei that coalesce to form a continuous film is a major factor determining film properties, that is, chemistry, short-range atomic order, crystallography, and microstructure.

The relative flux to the substrate was found to be controlled by:

1. Reactions at the target surface that affect the balance between the rate of removal of metal atoms and the rate of formation and removal of metal-oxide molecules.
2. Reactions at the substrate that affect the adsorption, surface diffusion, bulk diffusion, and desorption of metal atoms, metal oxide molecules, and atomic or molecular oxygen species.
3. Plasma volume reactions. Collisional and radiative processes that affect (a) either the oxidation of sputtered metal atoms, or the dissociation of sputtered metal-oxide molecules in the discharge, and (b) the creation of excited or ionized oxygen species in the plasma that ultimately engage in compound formation at either electrode.

Specific examples of each type of reaction and its influence on thin film growth in the yttrium-oxygen, zirconium-oxygen, and vanadium-oxygen materials systems will be given.

# Conductive-Polymer Films for Corrosion Protection

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Moderately conductive, electroactive polymer films may be used to hold a metal surface at an anodically protected potential. Such a film can, in principle, protect any portion of a metal sample with which it is in electrical contact, without need to cover the entire sample. This is a relatively new application of conductive polymers, and the prior literature is limited.<sup>1-4</sup> Deng, Smyrl and White reported an electrochemical study of poly(3-methyl thiophene) and titanium that addressed the underlying mechanism and the requirements for successful application.<sup>4</sup>

In our laboratory, we have taken an electrochemical approach to both film preparation and evaluation. We have concentrated on poly(3-methyl thiophene) (P3MT) films on stainless steel, mild steel and aluminum. Our approach has been to combine surface modification with electrodeposition to form stable and adherent films. The structure and performance of films has been correlated with deposition parameters to find an optimum preparation procedure. New efforts will include chemical modification of the films to improve reversibility and reduce the required mass and surface area of coating.

The mechanism of protection offered by electroactive polymers is anodic. A reversible electrochemical transformation between states of the film acts as a redox couple holding the polymer at a positive potential. Discharge of the redox couple balances the corrosion current of metal and holds the metal at a passivated potential, while the polymer is continuously recharged by reduction of dissolved oxygen. Its role is to mediate the metal/oxygen couple and stabilize the passive state. The film acts as a buffer, storing charge, and as an extended surface for oxygen reduction.

Material selection is based on the requirements of a suitable redox potential, environmental stability and reversibility to oxygen. P3MT is among the most stable conductive polymers in air and water environments. It has a rest potential near +0.6 V vs. NHE, well within the passive region for steel. P3MT, however, does not adhere well to smooth, passive metal surfaces. Deng et al. galvanically coupled titanium to films on glassy carbon. Our approach has been to modify the metal surface to accept a P3MT film. The metal sample is first anodized in phosphoric acid. A P3MT film is then electrodeposited onto the surface from a propylene carbonate solution. Control of current density and convection conditions are required to form a coherent film that covers the surface uniformly. This combination of surface modification and controlled deposition is a new strategy for meeting the material requirements.

Reduction of oxygen on the polymer must be sufficiently fast to support the corrosion current of the metal. Deng et al. enhanced the reversibility of P3MT films to oxygen by adding finely-divided platinum as a catalyst. To avoid use of platinum, we have explored the dependence of film performance on deposition conditions. Film formation proceeds by oxidation of monomer to a radical cation followed by reaction in solution. The overall reaction is an electro-oxidative polymerization. High current density and low convection rate maximize the concentration of radicals at the interface. The resulting high reaction rate gives a high efficiency of deposition, and it may also favorably influence microstructure. We find that the reversibility and charge capacity of the films increase with increasing current density and decreasing convection rate for a given charge passed. Thus, it is possible, to some extent, to improve kinetic performance by selection of optimal preparation conditions.

The next phase of this study will be to deposit P3MT films onto polymer-modified conversion coatings. Conversion coatings will be applied by the procedure given by Sugama and coworkers.<sup>5-7</sup> The conversion coat consists of a zinc phosphate layer interpenetrated by poly(acrylic acid) electrolyte bound to zinc ion. We expect that the PAA will provide a good site for adhesion of P3MT, and allow application of films to mild steel and aluminum.

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## States of Stress and Long Term Reliability

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X-ray diffraction methods, particularly using synchrotron radiation, can quantitatively determine the state of stress and the nature of defects in thin films and coatings in a non-destructive fashion. Various diffraction techniques can be used to image local defects and/or measure the state of stress over wide areas and for ranges of film thickness of 2.5 nm to tens of  $\mu\text{m}$ . The stress state in ultra-thin films can be assessed using precision rocking curve analysis. The ultrathin regime is of interest because the character of the growing film is usually established in the first few monolayers and the subsequent morphology determined by the signature of the early growth phase. Thicker films are readily studied, and the distributions of stress can be determined by mapping the quasi two-dimensional tensor strains determined by a method known as Bragg Angle Contour Mapping.<sup>1</sup> It is often thought that x-ray diffraction methods cannot be employed in the large deformation range, but this latter method has been used to study fatigue to 50,000 cycles on highly deformable materials by taking advantage of the high energy resolution of synchrotron radiation sources;<sup>2</sup> the technique readily applies itself to long term reliability studies of coatings.

The analysis of rocking curves, using a special high resolution, asymmetric, double crystal diffractometer, is capable of detecting strain displacements in the  $\Delta d/d \sim 10^{-7}$  range.<sup>3</sup> Figure 1 shows the change in lattice curvature as a function of coating thickness for W sputtered on Si(100) substrates. Figure 2 converts these observations to stress data using the standard Stoney equation approximation. It is noted here that a peak stress is reached in the range of 10 nm. The implications of this type of behavior on the growth and morphology of this type of film will be discussed.

A variety of high temperature films have been studied and several different classes of stress development have been found.<sup>4-7</sup> In certain cases the residual film stress starts small, grows to a peak stress, and then decays, as illustrated in Fig. 2. In other coating systems stress starts high and decays markedly with increasing film thickness, while in still other cases, the film stress grows linearly with film thickness. The implications of these findings on long term reliability will be discussed.

The BACM method of mapping strain distributions over wide areas will be described and the possibilities for using this technique to observe strain evolution for large scale fatigue applications will be developed. The ability to precisely quantitatively map strain fields in crystalline solids is a direct result of the availability of new high energy, high energy resolution, x-ray diffraction facilities at Synchrotron Sources. These provide the potential for knowing the state of stress for a wide variety of materials in thickness ranges from one monolayer to many millimeters.

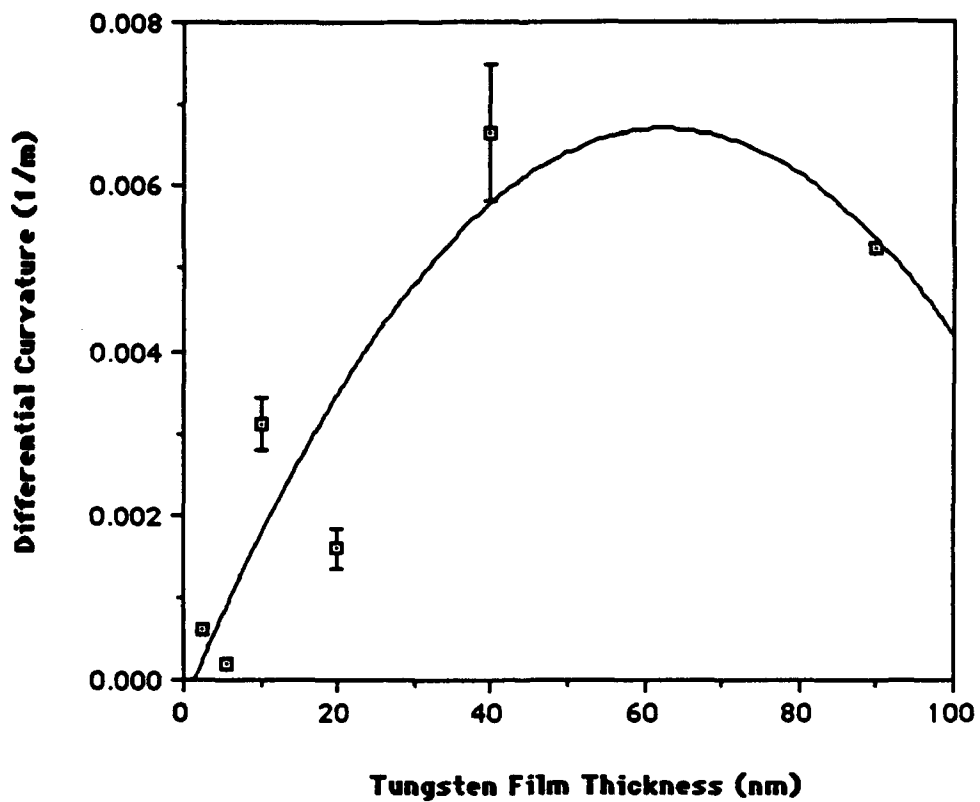


Fig. 1. Film Strain vs Thickness for Sputtered W.

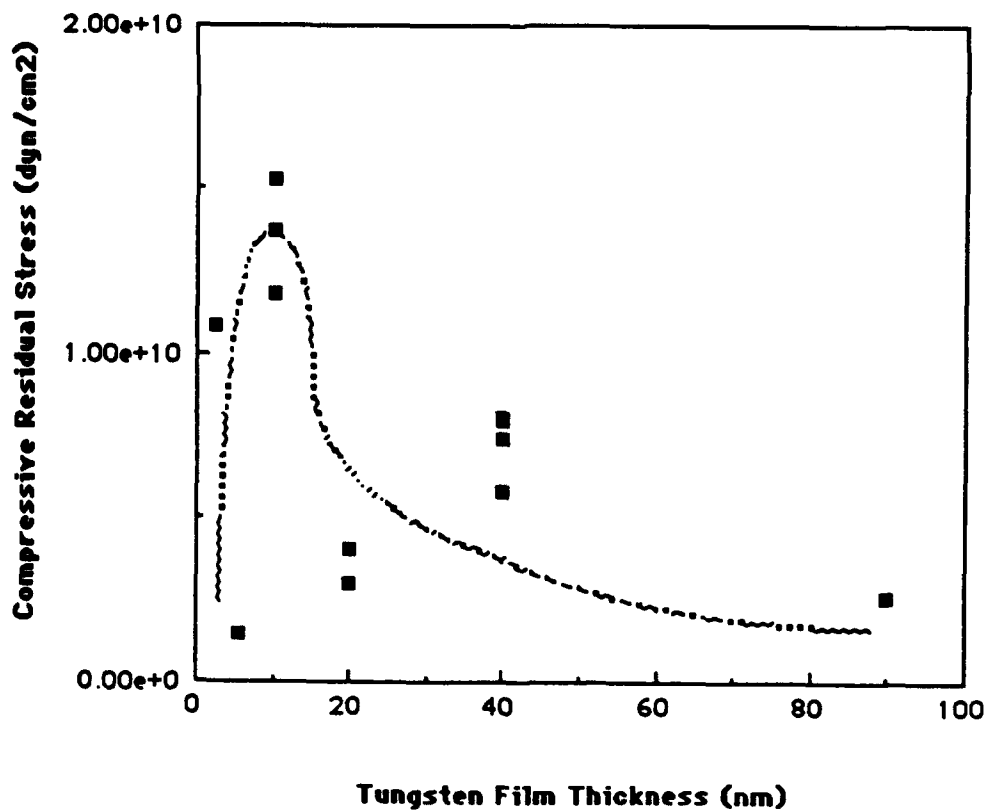


Fig. 2 Residual Stress vs Film Thickness



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# **Ion Implantation of a 4340 Steel for Hydrogen Resistance**

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A common failure mode for high strength steels used in stressed applications is Hydrogen Embrittlement. For fastener applications, coatings of Cd or Zn are used for corrosion protection of the steel. Hydrogen ingress into the steel may occur via a defect which is present in the coating or which may be formed when nuts are threaded onto bolts. In the latter case the torquing operation may remove the coating at local sites and expose the bare steel. Also a small crevice between the interfacing threads may be formed. In combination, these conditions may promote the occurrence of hydrogen embrittlement of the steel. It was recently demonstrated that the presence of a crevice at the root of a notch represented by a thread can decrease the tensile load carrying ability of ESR 4340 steel (HRC 52-55) by 30% at a 0.01 inch root radius, which is typical of machined thread root specifications. It was suggested that the presence of a crevice decreased the pH at the notch root and supplied extra hydrogen to induce a weakening in the material by hydrogen embrittlement. The intergranular fracture surface observed supported the suggestion that extra hydrogen was taken into the material during crevice corrosion at the notch root. Only a very small amount of hydrogen was required due to the high hydrogen sensitivity of this high strength steel.

As an alternative to applying a protective coating, ion implantation was selected because there is no discrete interface to fail since implantation occurs below the original surface. Also it is an environmentally clean technique with good directionality to penetrate to the base of notches and produce controlled subsurface changes. Hydrogen embrittlement cracks are known to initiate subsurface. Eventually the treatment, if successful, would be applicable to finished hardware.

For hydrogen to cause embrittlement, it must first enter the lattice and diffuse to a grain boundary at a site of high triaxial stress. Since interstitial diffusion is one method of hydrogen migration, nitrogen and boron were selected for implantation in order to block the interstitial paths available to the hydrogen. Another approach was to implant a species with a high recombination value for hydrogen. In this case the hydrogen would favor the formation of molecular gaseous hydrogen rather than entering the lattice in its atomic form. A decrease in the mobile hydrogen within the lattice should decrease the hydrogen embrittlement effect from the combination of a stress, exposure to an environment of 3.5% NaCl and the presence of a crevice.

The objective of this research was therefore to ion implant an electroslag remelted 4340 steel with a hardness of Rc 52-55 with nitrogen, boron and platinum. The region to be implanted was the notch in a round bar tensile sample and the surface of discs to be used for studies of mobile

hydrogen. The effect of ion implantation on mobile hydrogen after charging was measured along with the failure load after implantation to determine its effect on hydrogen embrittlement of high strength steels.

These data indicated that after hydrogen charging platinum decreased mobile hydrogen in the steel, while nitrogen and boron increased the amount of mobile hydrogen. The rate of electrochemical potential decrease to stable open circuit potential was also a function of implant species with platinum reducing the rate while nitrogen did not vary much from unimplanted steel. The boron implant decreased very rapidly to the open circuit potential. Mechanical testing in 3.5% NaCl showed that the platinum implant increased failure loads in comparison to unimplanted steel. The rate of voltage drop to open circuit conditions was a good measure of the susceptibility of the implanted steel surfaces to hydrogen embrittlement.

It is suggested that hydrogen recombination properties of the platinum and the electrochemical change of the surface in decreasing the rate at which open circuit potentials are reached both contributed to the increase in hydrogen embrittlement resistance for platinum. Both nitrogen and boron implanted steel showed increased mobile hydrogen pickup and decay rates to open circuit potentials which decreased their hydrogen embrittlement resistance.

# Solid Lubricant Characterization

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The thermal stability of various solid lubricant films is characterized by thermal desorption spectroscopy (TDS) with mass spectrometric detection of the evaporated species. TDS is useful in simulating the thermal decomposition, which can occur in an actual tribological environment since friction forces induce localized heating and the effects of adsorbed gases, film additives and impurities can be evaluated. In particular, TDS is used to help characterize sputtered MoS<sub>x</sub>, burnished MoS<sub>x</sub>, ion implanted MoS<sub>x</sub> and MoS<sub>2</sub> films.<sup>1-2</sup> The primary film decomposition products observed for the sputtered MoS<sub>x</sub> films were SO<sub>2</sub>, beginning at about 425 K and S<sub>2</sub>, beginning at about 1150 K. In addition, argon which is trapped in the film during sputter deposition is released from the sputtered MoS<sub>x</sub> film at various temperatures. Nitrogen ion beam modification of the sputtered films results in a decrease in the SO<sub>2</sub> production. Results from X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), wavelength dispersive spectroscopy (WDS), scanning electron microscopy (SEM) and Rutherford backscattering spectroscopy (RBS) were used to compliment the TDS spectra obtained in this work. Other techniques of use in solid lubricant characterization will also be mentioned.

A binding energy model<sup>2</sup> based on thermochemical and crystallographic data is used to provide insight into the thermal decomposition behavior of the MoS<sub>x</sub> films. For example, the model predicts the activation energy for the production of S<sub>2</sub> from MoS<sub>2</sub>, and the results agree with experimental measurements. Finally, the model will be used to predict the thermal stability for a series of solid lubricant systems.

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# Electroplating of Heat-Treatable Hard Chromium from a Mostly Trivalent Chromium Bath

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It has been shown that the current efficiency of chromium electroplating is increased by using methanol to produce some trivalent chromium in a hexavalent plating bath.<sup>1</sup> In recent studies, sufficient methanol has been used to convert at least 75% of the hexavalent chromium (130g Cr<sup>6+</sup>/liter) to the trivalent state. Additions of iron and sulfate were then made, and plating experiments were performed from two different bath formulations. The chromium, iron, and sulfate concentrations were:

<u>Bath</u>	<u>Total Chromium (g/l)</u>	<u>Iron (g/l)</u>	<u>Sulfate (g/l)</u>
1	7	2	30
2	90	7	130

Deposits 25  $\mu$ m thick were plated from each bath onto steel substrates. The current density and plating speed were:

<u>Bath</u>	<u>Current Density (A/cm<sup>2</sup>)</u>	<u>Plating Speed (<math>\mu</math>m/min.)</u>
1	0.3	1
2	0.075	0.1

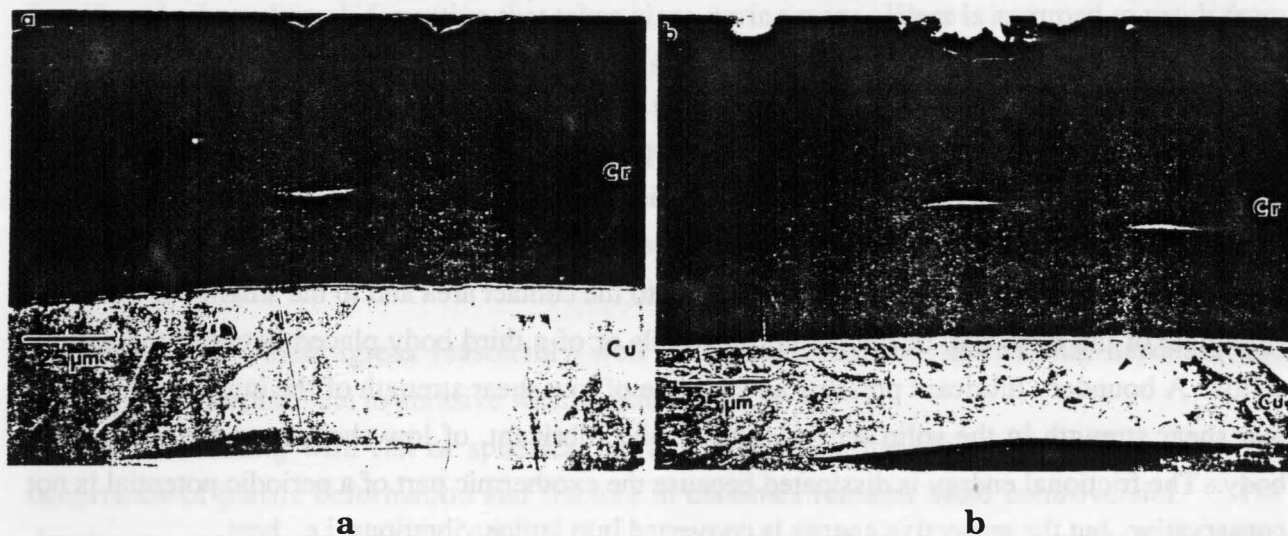
Chemical analysis showed that the deposits contain about 1% iron.

Microhardness tests were performed in the as-plated condition and after heating. The results were:

## MICROHARDNESS (KHN)

<u>Bath</u>	<u>As Plated</u>	<u>Heated 540°C</u>	<u>Heated 850°C</u>
1	760 (100g)	780 (100g)	---
2	1615 (50g)	1740 (50g)	890 (50g)

These results indicate that thick chromium deposits with unique response to heating can be plated from a largely trivalent bath. Fig. 1 gives examples of similar thick deposits on copper before and after heating.



**Fig. 1 Chromium plated on copper tubing.**

Plating thickness is more than 0.003 inches. The plating speed was about 10 microinches per minute. Both deposits contain about 1% Fe.

(a) As plated sample (KHN = 1025, 100g load).

(b) Heated 30 minutes at 1000°F after plating (KHN = 1920, 100g load).

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# Friction and Wear of Materials

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Friction and wear of materials are reviewed from a fundamental viewpoint, considering the various phenomena involved and the material properties that influence them. Friction and wear of materials are governed by contact mechanics, which involve predominantly plastic deformation in metals and elastic deformation and microfracture in ceramics. Friction is generally more difficult to understand in detail than wear. It is proportional to the contact area and to the smaller of the shear strengths: of the interface, of the sliding materials or of a third body placed between the sliding solids. A boundary lubricant presents an example of low shear strength of the interface, teflon of low shear strength in the solid second, and a solid lubricant, of low shear strength in the third body. The frictional energy is dissipated because the exothermic part of a periodic potential is not conservative, but the respective energy is converted into lattice vibrations, i.e., heat.

Wear is the response of the materials to the contact stresses and to the environment. Wear rates and wear mechanisms depend on the material properties of the sliding solids. We shall examine wear from the viewpoint of mechanical properties first, then we shall consider the influence of chemical properties on wear. We shall concentrate our attention on ceramics, whose successful application still demands better tribological understanding based on material properties.

## MECHANICAL ASPECTS OF WEAR

Ductile materials wear mostly by plastic deformation and their wear volume is expressed<sup>1</sup> by the general equation

$$V = k \cdot \frac{L}{H} \cdot s \quad (1)$$

where  $k$  is the dimensionless wear constant,  $L$  the load pressing the surfaces together,  $H$  the hardness of the softer material and  $s$  the sliding distance.

In abrasion, indentation of the material is caused by sharp edges of the hard abrasive; in sliding wear, the contact is extended over a large enough area to produce relatively low average stresses; and in rolling service, the contact stresses are large, but friction forces are low.

A notable feature of abrasive wear in ceramics<sup>2</sup> is a dependence of the wear mechanisms on the size of the abrasive particles: abrasion by fine particles is smooth and occurs by plastic deformation, but severe abrasion is accompanied by fracture. This is explained by the indentation studies of Lawn and coworkers<sup>3</sup> who found that, in order to form a crack, an

indentation must be large enough so that the stress intensity factor  $K_I = \sigma \sqrt{a}$  formed by the indentation stress  $\sigma$  (hardness) and the size of the indent  $a$  exceeds the toughness  $K_{Ic}$  of the material.

An equation for the abrasive wear of ceramics has been derived by Evans and Marshall.<sup>4</sup> It is based on the lateral crack formation that takes place during wear. Wear is assumed to result from the extension of the lateral cracks as the indenter slides along the surface to produce a scratch. This model assumes a purely brittle form of wear. It predicts that the wear volume varies with the normal force  $P$ , hardness  $H$  and toughness  $K_c$  as

$$V = \text{Const. } p^{7/6} \cdot H^{-1/2} \cdot K_c^{-2/3} . \quad (2)$$

This equation, which agrees reasonably well with measurements, shows that hardness and toughness both contribute to abrasive wear resistance.

In pure sliding with flat or spherical contact, which are the geometries of bearings, the occurrence of plastic deformation and fracture in ceramics remains more controversial.<sup>5-6</sup> The dominant wear mechanism in silicon nitride is microfracture, as demonstrated by high-magnification surface topography.<sup>6</sup> If this is the case for all brittle materials, toughness should be the main determinant of wear resistance. This was verified in the case of zirconia which can be prepared with a toughness varying from 2 to 11.5 MPa $\sqrt{m}$  and constant hardness by doping with various amounts of yttria.<sup>7</sup> The wear resistance of these materials increases with the fourth power of toughness (by a factor of 1200 when toughness increases by a factor of 6). In transformation-toughened zirconia, cleanly cut grooves on the surface worn in air (relative humidity 50%) attest to plastic deformation. Obviously, the contributions of fracture and plastic deformation to wear of ceramic materials depend on the combination toughness and hardness of the material.

An interesting feature of ceramic wear is its dependence on the load. Wallbridge and coworkers<sup>8</sup> found very low wear rates for alumina sliding against itself or against ultrahigh-molecular-weight polyethylene; the contacting surfaces were relatively large (hundreds of mm<sup>2</sup>) and the loads were modest, so that the contact stresses were low. Deckman and coworkers reported an abrupt increase in sliding wear of alumina by as much as two orders of magnitude above a critical load,<sup>9</sup> below this transition, the wear rate increases with the fifth power of the load. In sliding wear of zirconia, the wear rate of a spherical slider decreases as the macroscopic contact surface is increased by wear; this can be interpreted to mean that the wear rate varies with the third power of the average contact stress.<sup>7</sup>

In rolling service, experience has shown that silicon nitride performs much better than other ceramics. The relevant mechanical properties are the strength of this material, which allow it to sustain without damage the high contact stresses of the rolling contact and its outstanding fatigue resistance. Habeeb et al.<sup>10</sup> tested alumina with the contact stresses representative of ball bearings



and reported catastrophic wear. Kim and coworkers<sup>11</sup> found that the wear rate,  $w$ , of a number of ceramics in rolling wear could be expressed by the formula

$$w = \frac{dV}{dx} = \alpha (P_m \sqrt{R_{\max}/K_{1c}})^{5.46} \quad (3)$$

where  $P_m$  is the average macroscopic Hertzian contact stress,  $R_{\max}$  the average maximum surface roughness and  $K_{1c}$  the toughness of the material. The inclusion of the surface roughness illustrates how the contact stresses are determined by the wear process.

When ceramics are used in contact with metals, hardness is determinant. Metals deform plastically in the contact<sup>1</sup> and do not generate sufficient contact stresses to induce wear by fracture in the ceramic. In unlubricated service, wear usually causes transfer of metal onto the ceramic surface. The latter wears either by fatigue or, more often, by tribochemical reaction with the metal and the environment. An illustration of this phenomenon is the dissolution of diamond when one attempts to use it for cutting steels.

### TRIBOCHEMICAL EFFECTS

An outstanding property of ceramics is their corrosion resistance and their chemical inertness. It was somewhat of a surprise when early researchers uncovered a strong influence of the chemical environment, especially the ambient humidity, on the wear of ceramics even at room temperature.<sup>5,12</sup> The wear rate of silicon nitride decreases by two orders of magnitude when the relative humidity of argon and of air is increased from 0 to 100%. Sliding in dry argon is accompanied by purely mechanical wear that consists of microfracture.<sup>6</sup> When sliding occurs in humid argon, the wear track is smooth and the wear debris are predominantly amorphous with dispersed fine crystallites a few nanometers in size. The amorphous material is a silicon oxide and the crystallites are silicon nitride. Sliding in water produces ultra-smooth surfaces that allow hydrodynamic lubrication by a water film with very low friction at low velocities (6 cm/s) at high bearing pressures (100 MPa).

The oxides formed on ceramics can act as lubricants under the right conditions. In silicon nitride, we have been able to obtain a friction coefficient as low as  $\mu = 0.05$  when the surfaces were made ultraflat by the reaction with water just described above. At high temperatures, sliding in humid air produces low friction and low wear. This self-lubricating phenomenon operates at temperatures up to 650°C: at higher temperatures water vapor does not adsorb on the surface. Alumina sliding in water forms a lubricating hydroxide that reduces friction to 0.3. Other schemes for lubrication at extreme temperatures are being developed; these are the supply of lubricant additives through a gas<sup>13</sup> and the deposition of carbonaceous layers by catalytic decomposition of hydrocarbons.<sup>14</sup>

The chemistry of zirconia is very different from that of silicon nitride, and the chemical effects on friction and wear are correspondingly different. Sliding in humid air and in water<sup>7</sup> causes an increase in the wear rate of zirconia of about a factor of 10 in the case of zirconia. The phenomenon responsible for this increase in wear is chemisorption embrittlement. It is not surprising that alumina responds to humidity by an increase in the wear rate, just as zirconia does, since it is known to be susceptible to stress corrosion cracking.

## WEAR OF LUBRICATED CERAMICS

Lubricants perform two essential functions: hydrodynamic lubrication at high speeds and low loads and boundary lubrication at low velocities and at high loads. Since hydrodynamic lubrication is the physical separation of the sliding surfaces, it does not depend on the material properties of the solids. Polar hydrocarbons adsorb on metal surfaces and lower the friction coefficient to  $\mu < 0.1$  by boundary lubrication. Chemically inert hydrocarbons do not provide boundary lubrication of metals; in slow sliding, the friction coefficient for metals is  $\mu = 0.7$ . In the case of ceramics, chemically inert hydrocarbons, such as paraffin, act as boundary lubricants, resulting in a friction coefficient  $\mu = 0.12$ . We do not know the reason for the chemical lubrication of paraffins with ceramics. We speculate that the same acid and base sites on ceramics that are responsible for the catalytic activity of these materials in hydrocarbon cracking and isomerization are also responsible for the chemisorption of paraffins. Boundary lubrication invariably causes a sizeable decrease in the wear rate of metals. With ceramics, this has been obtained with silicon nitride, but not with alumina and toughened zirconia. In general, one observes that ceramics which wear rapidly in dry sliding show decreased wear by boundary lubrication and that ceramics that wear slowly in dry sliding experience an increase in wear rate with boundary lubricants, predominantly through chemisorption embrittlement.

For metals, antiwear lubricants are used industrially. They are based on the elements sulfur and phosphorus. These are well known solid state surfactants: they adsorb strongly on surfaces and render them chemically inert. Chlorine is the basis for "extreme pressure" additives, dissolving nascent metallic junctions. No effective lubricant additives are known for ceramics yet, their future development depends on a more thorough knowledge of the tribochemistry of these materials.

Thus, the tribological technology is well developed for metals; the successful application of novel materials will require new mechanical designs and lubricant chemistries adapted to their different mechanical and chemical properties.

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## Modulated Ceramic Coatings

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Ceramic coatings with predesigned microstructures and controlled variations in composition have been synthesized by chemical vapor deposition in computer-controlled reactors.

Methodologies to produce fine-grained deposits have been developed either by introducing dopants at regular intervals to enhance nucleation of new grains or by simply pulsing the reactant gases in fully miscible systems such as TiN-TiC. In this system, the 4% difference in lattice parameter between the two compounds was sufficient to promote nucleation of new grains of one compound on the other with little or no diffusion at the interface. The development of a columnar structure which is endemic in most CVD materials was thus avoided. Judicious selection of timing sequences led to the formation of ultrafine microstructures while the average stoichiometry of the layered deposits could be varied from  $\text{TiC}_{0.95}\text{N}_{0.05}$  to  $\text{TiC}_{0.05}\text{N}_{0.95}$ . The same methods have been applied to the production of graded materials with predetermined profiles. These structures may improve the adhesion of thick deposits since key properties can be varied gradually. The technique could also be used to deposit materials incompatible with the substrate, a serious drawback in most deposition technologies.

Filaments of silicon carbide and titanium carbide as small as 100 to 200 nm in diameter were grown by the vapor-liquid-solid mechanism on arrays of transition metal catalytic particles deposited on graphite substrates. The resulting skeletal structure of filaments were subsequently infiltrated *in situ* by titanium nitride under different process conditions. The filament-reinforced composites exhibited a matrix of ultrafine grains and little or no crack formation, as compared to monolithic deposits of the constituent phases.

The extension of these processing methodologies to other systems will be discussed. Potential applications of these deposits in tribology and for corrosion protection will be reviewed.

# **Excimer Laser Surface Processing of Metals and Ceramics for Tribological Applications**

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The use of excimer lasers for the modification of metal and ceramic surface alloys opens a range of processing techniques which offer the precision of ion beam mixing techniques but at much higher processing rates. In addition, excimer laser surface processing offers the possibility of new surface modification technologies. Most metals have low reflectivity in the UV so laser light is coupled strongly to the surface. The short pulse length of these lasers, along with a shallow absorption depth, results in a heated zone which is also quite shallow. Modest fluences are sufficient to melt this surface zone. Quench rates from the melt are high enough to bypass equilibrium processes and form metastable phases in some materials. Mixing by liquid phase diffusion between layers of vacuum evaporated materials or zone refinement occur during the melt duration. Because of the short melt duration the amount of mixing can be controlled by the use of multiple melt resolidification events. These techniques make available a large range of surface alloy compositions on engineering materials.

The strong bonding between the surface layer and the substrate which results from melting and mixing suggests that this technique is well suited to tribological applications. We have examined the tribological properties of surfaces in a number of systems including metal, ceramic, oxide, and solid lubricant films. A suggestion of the possibilities inherent in the process will be presented.

# **Corrosion Protection of Al Alloys and Al-based Metal Matrix Composites**

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Corrosion protection of Al alloys and Al-based metal matrix composites (MMCs) by conversion coatings, anodized layers, chemical passivation in  $\text{CeCl}_3$  and polymer coatings has been evaluated in 0.5 N. NaCl by electrochemical impedance spectroscopy (EIS). A commercial chromate conversion coating (Alodine 600) provided corrosion protection for Al/SiC and Al/Gr MMCs, but was not as effective as for Al 6061. For Al/SiC, it was observed that sulfuric acid anodizing did not produce the corrosion resistance obtained for Al 6061. The corrosion resistance for hard anodized Al/SiC was less than that for conventional anodized Al/SiC. This unusual result is due to the presence of the SiC particulates and has been explained by a new model for the formation of anodized layers on Al/SiC. For Al/Gr, difficulties were encountered with the sulfuric anodizing process. As long as graphite was exposed in defects of the Al 6061 face sheet during anodizing, the proper anodizing conditions could not be reached. Increased thicknesses of Al 6061 face sheets on Al/Gr have been suggested for anodizing coatings to enhance the corrosion resistance.

Significant improvements of the corrosion resistance by chemical passivation in  $\text{CeCl}_3$  have been observed for Al/SiC and Al/Gr. Chemical passivation in  $\text{CeCl}_3$  for 7 days provided better corrosion resistance for Al/SiC and Al/Gr than chromate conversion coatings (Alodine 600) or sulfuric anodizing. A comparison with the improvement of the corrosion resistance of Al alloys and Al-based MMCs by treatment with chromate conversion coatings shows that chemical passivation provides a valuable alternative to chromate conversion coatings.

Polymer coatings and a combination of chemical passivation in  $\text{CeCl}_3$  and a polymer coating provided excellent corrosion resistance for Al/SiC and Al/Gr. An accelerated corrosion test for polymer coatings has been developed to evaluate the quality and to predict the lifetime of coatings in a short time using EIS.

In more recent work, attempts have been made to shorten the passivation time in  $\text{CeCl}_3$ . Very promising results have been obtained for Al 6061 by immersion in hot  $\text{Ce}(\text{NO}_3)_3$  for 2h followed by immersion in  $\text{CeCl}_3$  for 2h. Additional improvements can be achieved by adding an anodic polarization step in deaerated 0.1 M  $\text{Na}_2\text{MoO}_4$ . Samples treated by the  $\text{Ce}(\text{NO}_3)_3/\text{CeCl}_3/\text{Na}_2\text{MoO}_4$  process did not show any signs of corrosion during immersion in 0.5 N NaCl for 60 days. Polarization tests suggest that surfaces treated in this new process behave like insulators supporting neither anodic or cathodic processes.

EIS is a powerful tool to monitor the passivation process in  $\text{CeCl}_3$  and the corrosion behavior during subsequent exposure to NaCl. Pitting and crevice corrosion of Al alloy and Al-based MMCs can be detected by characteristic changes in the low frequency range of the impedance spectra. The analysis of the impedance spectra allows us to determine pit growth rates at the corrosion potential.

#### ACKNOWLEDGEMENT

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## **Ion-Induced Disorder in Ceramics**

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Modification of the mechanical properties of ceramic surfaces by ion-implantation has been investigated as a means of improving the hardness and wear-resistance of such materials. We review the Oak Ridge National Laboratories studies and our Cornell work on MgO and Y<sub>2</sub>O<sub>3</sub>-stabilized cubic ZrO<sub>2</sub>. Three regimes of hardness versus ion-fluence have been identified; a region where the hardness increases with fluence, this region has been associated with a damaged but essentially crystalline microstructure, upon reaching some maximum hardness value the hardness then decreases with further increase in ion fluence, this has been attributed to sub-surface amorphization and then as the amorphous layer thickens, absolute softening has been observed.

Two techniques have primarily been used to study the microstructure following implantation—transmission electron microscopy (TEM) and ion-beam channeling, a variation of Rutherford backscattering spectrometry (RBS). RBS is relatively easy and, in most cases, the technique is non-destructive; also, no specimen preparation is required prior to examination. RBS enables the concentration of implanted species and the damage (structural disorder) to be determined as a function of depth. However, since the technique requires that the specimen be planar and uniform within the area of the analyzing beam, which is generally on the order of 1 mm<sup>2</sup>, small localized structural changes and precipitates may not be detected. TEM using plan-view and cross-sectional specimens has been less widely used for two reasons: the microstructural changes occur at or near the surface which makes specimen preparation difficult and during the preparation of TEM specimens damage may be introduced.



# Neutron Energy Loss Spectroscopy for Nondestructive Analysis of Hydrogen in Metals

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## INTRODUCTION

The objective of this research is to experimentally and theoretically evaluate nondestructive methods for determining the total hydrogen in metals at the atom parts per million level. The techniques being studied rely on differences in neutron energy loss when scattering off of host metal nuclei versus hydrogen nuclei. Neutron scattering with light nuclei, such as hydrogen, result in large neutron energy losses per scatter and in unique energy/angle relationships. Heavy nuclei such as iron, zirconium, copper, manganese, etc., result in small energy losses and nearly isotropic scattering. These differences can be measured and used to nondestructively measure hydrogen content.

## IRON FILTERED BEAM TECHNIQUES

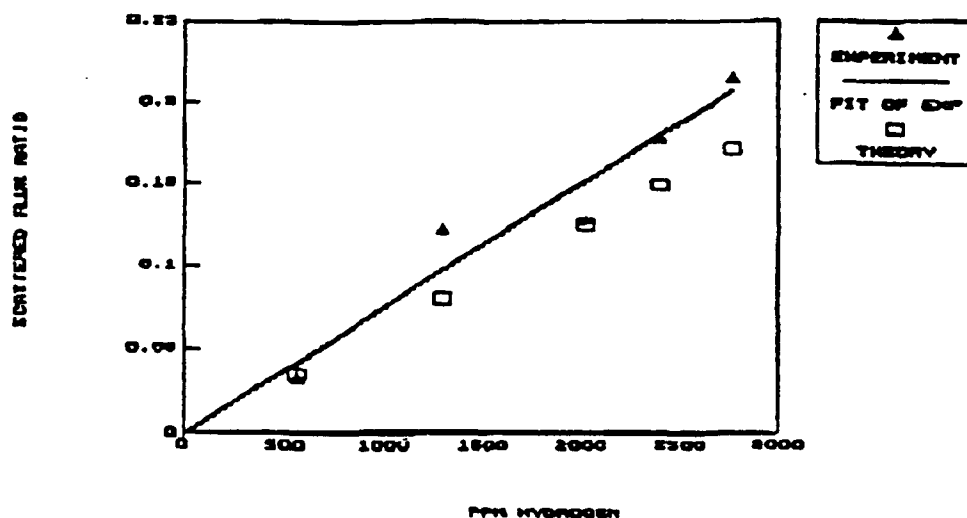
Two techniques are currently under investigation. The first utilizes a beam of neutrons that has been filtered by iron.<sup>1</sup> The cross-section for iron exhibits a deep minima at 24 keV, resulting in a penetration window for neutrons. This creates a nearly monoenergetic beam of 24 keV neutrons that will penetrate through steel specimens with a relatively small amount of scattering from the iron nuclei in the specimen. Some multiple scattering will occur that will isotropically scatter neutrons with energies above about 15 keV.

If hydrogen is present in the sample, however, there exists a unique scattering angle vs. energy loss relationship as described by the collision of two hard spheres of equal mass. When the neutron scatters off of a hydrogen nucleus, there is appreciable energy loss at large scattering angles. These neutrons appear at energies less than 15 keV for scattering angles greater than approximately 40 degrees. Thus, it is possible to measure the amount of hydrogen in a sample by measuring the neutron spectrum at a scattering angle greater than 40 degrees. The measured neutron spectrum at this point will contain a background of iron scattered neutrons at energies below 24 keV (but above 15 keV) and neutrons at specific energies below 15 keV depending upon the scattering angle chosen.<sup>2</sup>

To test this technique both theoretical calculations and experimental measurements have been completed. Monte Carlo techniques have been used to theoretically model the problem.<sup>3</sup> A 2.0 cm diameter LND proton recoil detector<sup>4</sup> is used to measure the neutron spectrum. The detector is

operated at a pressure of 4 atmospheres with a gas composition of 99% hydrogen and 1% methane quench gas. The detector includes a gamma-ray discrimination system to eliminate gamma-ray induced pulses from the neutron spectrum.<sup>5</sup> The proton recoil spectra are unfolded using SPEC4 to determine the energies of scattered neutrons intercepted by the detector.<sup>6</sup> These experimental measurements have been carried out on the "F" beamtube at the University of Missouri Research Reactor (MURR).

Figure 1 shows a comparison of theoretical and experimental results. The sample was a semi-sphere of iron powder filled to various pressures of hydrogen gas. All results are expressed in atom ppm. As can be seen, there is excellent agreement between experimental and theoretical measurements, although experimental errors indicate a lower level of detection of approximately 500 atom ppm with the current system. Improvements in the system could reduce this sensitivity to less than 100 atom ppm.



**Fig. 1 Hydrogen/Iron Scattered Flux Ratio**

### NOTCHED FILTER TECHNIQUES

The notched filter technique<sup>7-8</sup> uses a filtered spectrum of neutrons that has been depleted of neutrons in given energy ranges by absorption at resonance energies by a thick resonance absorber. This spectrum is then detected by thin foils using the same resonance absorber. Theoretically, the resulting activation in the foils should be zero unless a sample placed in the notched neutron spectrum slows neutrons down to a resonance energy so they can activate the foil. If the sample material has a large atomic number, i.e., iron, zirconium, copper, manganese, or other metal, the amount of slowing down and resulting activation is small. If the sample has hydrogen in it, the slowing down of the neutrons is large and causes activation. Thus, this technique, similar to the one discussed above, utilizes the appreciable energy loss of neutrons scattering off of hydrogen nuclei.

In the past, the application of this technique has utilized a large, planar source of filtered neutrons to measure hydrogen content in zirconium.<sup>7-8</sup> An improvement in sensitivity can be realized by utilizing beam geometry such as that available at the "F" beamtube at the MURR. This reduces the amount of background activation and increases the sensitivity for the detection of hydrogen.<sup>9</sup>

In practice, indium, which exhibits several resonances in the 1 to 10 eV energy range, is used for the neutron filter and the activation foils. These foils are subsequently counted on large volume NaI, gamma-ray detectors. Experimental measurements have been completed at the "F" beamtube at the MURR and have been compared to the results from a simple theoretical model. The results are summarized in the table below as signal to noise ratios. The signal is activation of foils due to neutron energy loss from hydrogen scattering, and the noise is due to iron scattering.

**TABLE 1**  
**Signal to Noise Ratios**

Sample	Theoretical		Experimental	
	<u>Planar Source</u>	<u>Beam Source</u>	<u>Planar Source</u>	<u>Beam Source</u>
0.25" 10,000 ppm	1/3	1/0.3	1/7	1/2
0.10" 1,000 ppm	1/60	1/3		
0.10" 100 ppm	1/1850	1/50		

The comparison of the theoretical results using the planar source vs. the beam source gives an indication of the improvement that can be achieved by using the beam geometry with the notched filtered technique. As the sample becomes smaller and the hydrogen concentration becomes less, the improvement increases. The experimental results show similar improvements, although the signal to noise ratio is worse due to activation by background neutrons in the experimental area.

Although these results are preliminary, the experimental evidence indicates it is possible to detect approximately 500 atom ppm of hydrogen. Future improvements should lower this sensitivity to less than 10 atom ppm.

## CONCLUSION

Two nondestructive techniques utilizing neutrons have been studied for measuring hydrogen in metals. Both detect the total amount of hydrogen present in the sample, as opposed to the mobile hydrogen.

The iron filtered beam technique has a demonstrated sensitivity of approximately 500 atom ppm and is applicable only to steels. This limitation is primarily due to counting statistics in the proton recoil spectrometer and can be improved by the fabrication of a large area detector. This technique is most applicable to large samples. The combination of relatively large samples (on the order of a few centimeters) and a large area detector system should lower the sensitivity to less than 100 atom ppm.

The notched filter technique has also been demonstrated and appears to have a lower sensitivity. It is applicable to any metal. It is less applicable to large samples, working most effectively with samples a fraction of a centimeter thick. It has demonstrated sensitivity of 500 atom ppm that could ultimately be reduced to less than 10 atom ppm.

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## Electrodeposition from Supercritical Electrolytes

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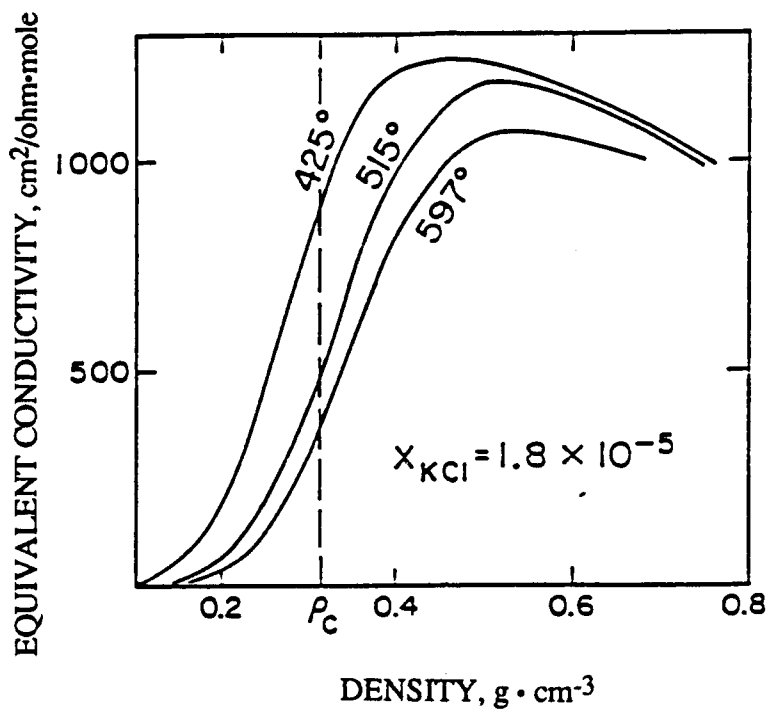
We are currently investigating the feasibility of depositing metals from mixed, organic, supercritical electrolytes. We are focussing on developing processes for hard-to-plate metals such as aluminum and titanium. Research in the area of deposition from nonaqueous solvents began early in this century,<sup>1</sup> and subsequent research advances have resulted in at least one commercial process for the deposition of aluminum.<sup>2</sup> A number of studies have been carried out on the deposition of aluminum from aromatic hydrocarbons.<sup>3</sup> Aluminum is an outstanding coating material for many applications. It is ductile and has good electrical and thermal conductivities. Its coherent oxide film makes it corrosion resistant, and its corrosion resistance can be further increased through anodizing.

The properties of supercritical electrolytes have been investigated, primarily by physical chemists, over the past 30 years. Franck<sup>4</sup> observed an equivalent conductivity of approximately  $1200 \text{ cm}^2/\text{ohm-mol}$  for a dilute, supercritical, aqueous KCl solution (Fig. 1). Bard and coworkers<sup>5</sup> measured the diffusivities of various species in supercritical water and ammonia as a function of temperature. They determined that the diffusivity deviates positively from that predicted by the Stokes-Einstein model as the critical temperature is approached (Fig. 2). They conjectured that the increased diffusivity resulted from reduced ion solvation under supercritical conditions. Because the solvent must be able to release the ion during deposition, such an effect would be beneficial. In addition, supercritical solvents offer the possibility of operating over a wide range of temperature and pressure.

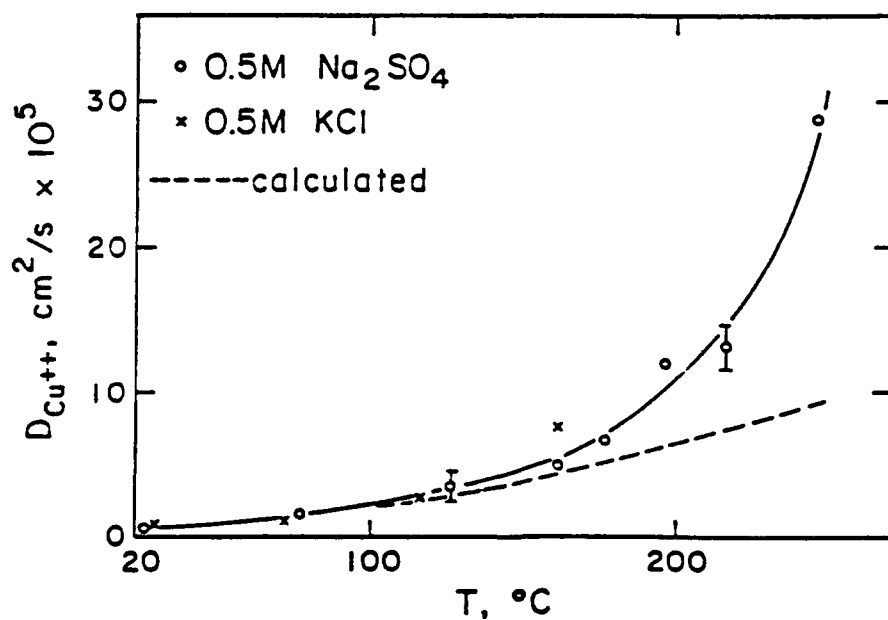
We first demonstrated a potential commercial process using supercritical electrolytes in our laboratory.<sup>6</sup> We synthesized dimethyl carbonate from carbon monoxide and methanol in carbon dioxide cosolvent at  $90^\circ\text{C}$ . The phase behavior of this solvent system is shown in Fig. 3. In a study related to the transport properties in this solvent system, we measured the dielectric constant of the supercritical fluid using a radio frequency reflection technique.<sup>7</sup>

Our current efforts are directed towards studying a system for use in the electrodeposition of aluminum. We are considering the toluene-aluminum bromide system that was used successfully in Gileadi's laboratory under subcritical conditions. Because the critical temperature of toluene is relatively high, we are using  $\text{CO}_2$  as a cosolvent. We plan to use a mixture of components that will give us an operating temperature near  $100^\circ\text{C}$ . At present we are determining the phase behavior and transport properties of several solution compositions.

In future work we plan to perform studies of electrodeposition of other hard-to-plate metals such as titanium, molybdenum, and zirconium. In addition to metal deposition, similar processes could lead to new techniques for producing materials such as alloys and thin film semiconductors.



**Fig. 1. Equivalent conductivity vs. density for a dilute aqueous solution of KCl in supercritical water.**



**Fig. 2. Diffusivity of cupric ions in near-critical water.**

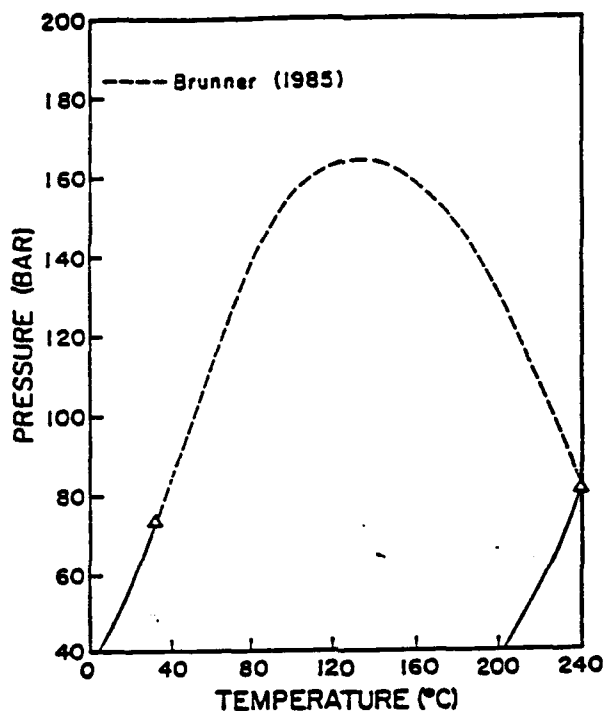


Fig. 3. Phase behavior of the methanol-CO<sub>2</sub> system.

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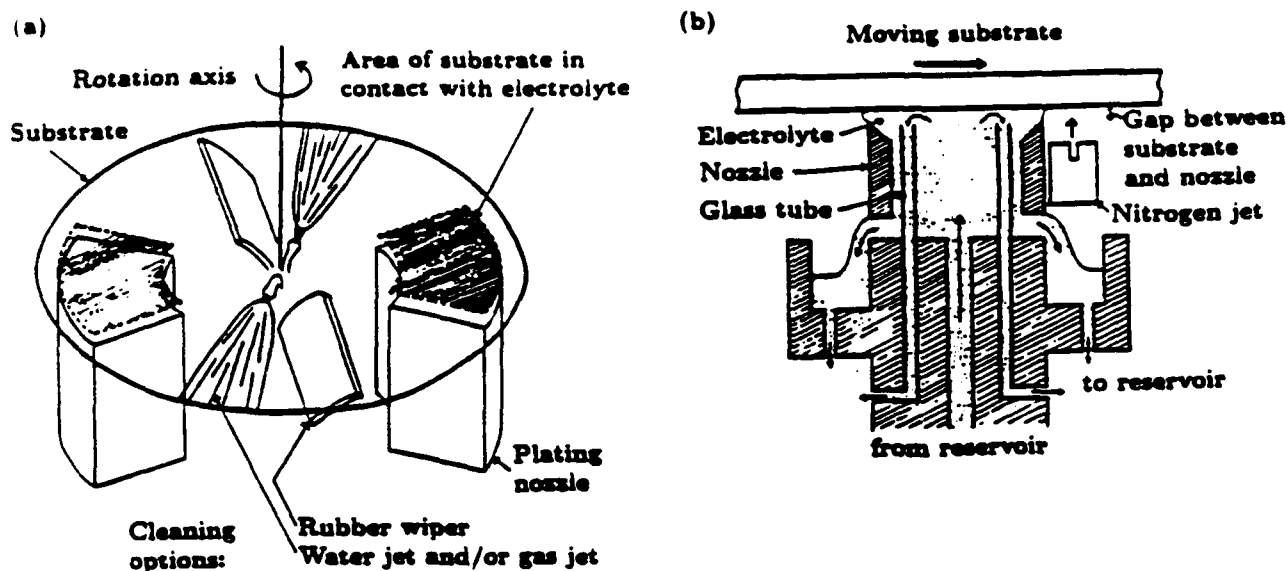
## Electrodeposition of Multilayer Thin Films

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Multilayered thin films, consisting of fine alternating layers of two different materials, have far-ranging applications including x-ray mirrors and magneto-optical storage media. These films are commonly made by vacuum processes such as sputtering or evaporation, but may also be made by electrodeposition which can be a faster and more economical method. Multilayers may be electrodeposited from a single plating solution containing two ionic species, using a periodically varying potential,<sup>1-8</sup> or from two different plating solutions by transferring the substrate between them. This latter method has been used to successfully fabricate Ni/NiP<sub>x</sub> and NiP<sub>y</sub>/NiP<sub>x</sub> multilayers with repeat lengths (periods) as low as 20Å,<sup>9-14</sup> where  $0 < y < x = 25\text{at.\%P}$ . NiP<sub>y</sub> is crystalline for low phosphorus contents but amorphous above  $y = 18\text{at.\%}$ , so that fully crystalline, fully amorphous and crystalline-amorphous multilayers can be made. The phosphorus content of the alloy depends on both the chemistry of the plating solution and the plating current density, and falls as the current density increases, allowing control over the film composition.

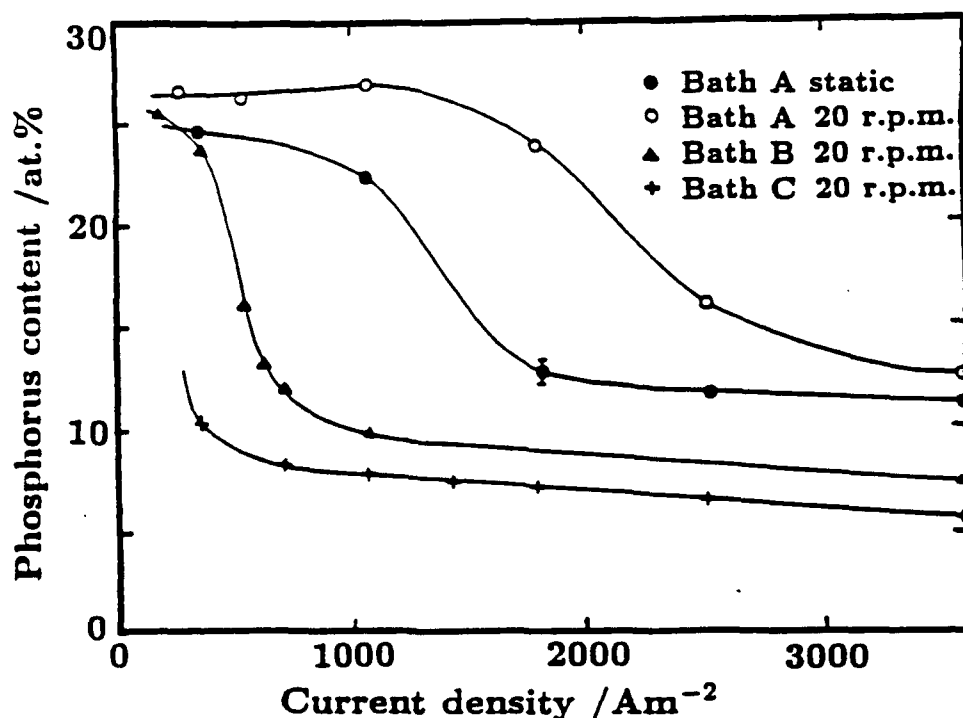
The multilayer films are characterized using x-ray diffraction and cross-sectional TEM to obtain values for the repeat lengths and interface diffuseness (typically 6-9Å). From the decay on annealing of the low-angle x-ray peaks corresponding to the composition modulation, the diffusivity of phosphorus in the multilayer can be measured to high precision.<sup>15</sup> Fully amorphous films show a diffusivity which decreases continuously with time as the as-deposited metastable structure relaxes and becomes denser. The structural relaxation has also been measured from changes in the internal stress in the films, using a bending beam technique. The structural relaxation causes a densification and therefore an increase in the tensile stress in the film. In fully crystalline or crystalline-amorphous multilayers, x-ray results indicate that phosphorus diffuses into the grain boundaries of the low-phosphorus layers of the multilayer to an extent depending on temperature. Results for the diffusivity of phosphorus in the multilayers will be presented and related to the effect of annealing on the internal stress and saturation magnetization, which can be used as a sensitive measure of the phosphorus distribution within the layers. Finally, the application of electrodeposition as a general method for making multilayered thin films will be discussed.



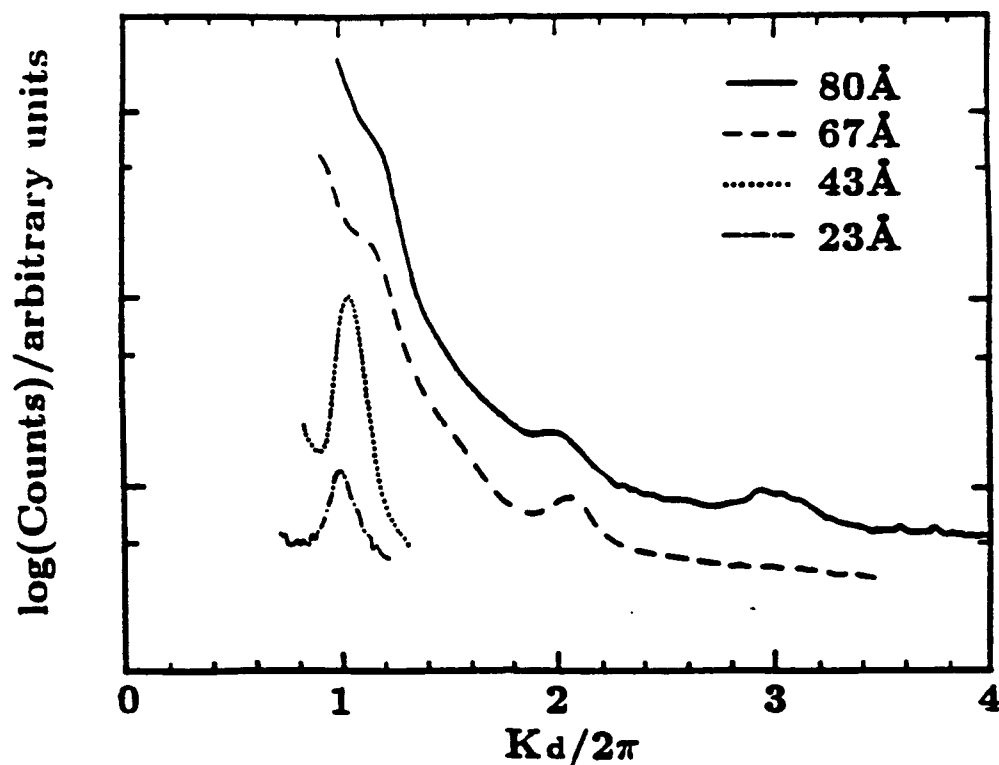


**Fig. 1. Representation of the dual bath plating apparatus used to make the multilayers.**

(a) A circular substrate rotates horizontally over two plating nozzles and is cleaned by water or gas jets or a rubber wiper. (b) Cross-section of a plating nozzle. The substrate is supported just above the two nozzles and is rotated by a motor. Plating solution is pumped up through the nozzles and makes contact with the substrate in a wedge-shaped region, over which plating occurs. As the substrate rotates, a multilayer is built up. The substrate is cleaned, as shown in (a), to avoid cross-contamination between the solutions. From Ref. 11.



**Fig. 2. Composition of NiP<sub>x</sub> deposits from different plating solutions as a function of plating current and rotation speed of the substrate.** The solutions A, B, C contain decreasing amounts of phosphorus. From Ref. 11.

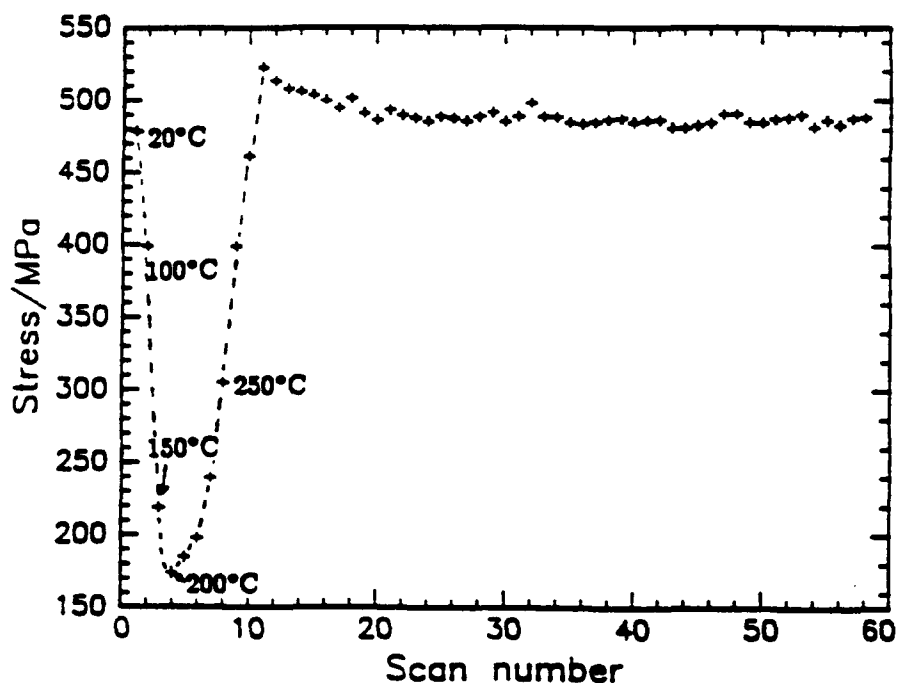


**Fig. 3.** Low angle x-ray traces from three Ni/NiP<sub>x</sub> multilayers of repeat lengths 23, 43 and 80 Å and one NiP<sub>x</sub>/NiP<sub>y</sub> multilayer of repeat length 67 Å. (Ref. 11) The vertical scale is offset and the horizontal scale is plotted as  $Kd/2\pi$  where  $d$  is the repeat length of the multilayer and  $K = 2k \sin \theta$ , with  $k$  the x-ray wavenumber and  $\theta$  the diffraction angle. The horizontal scale is therefore equivalent to the order of reflection.



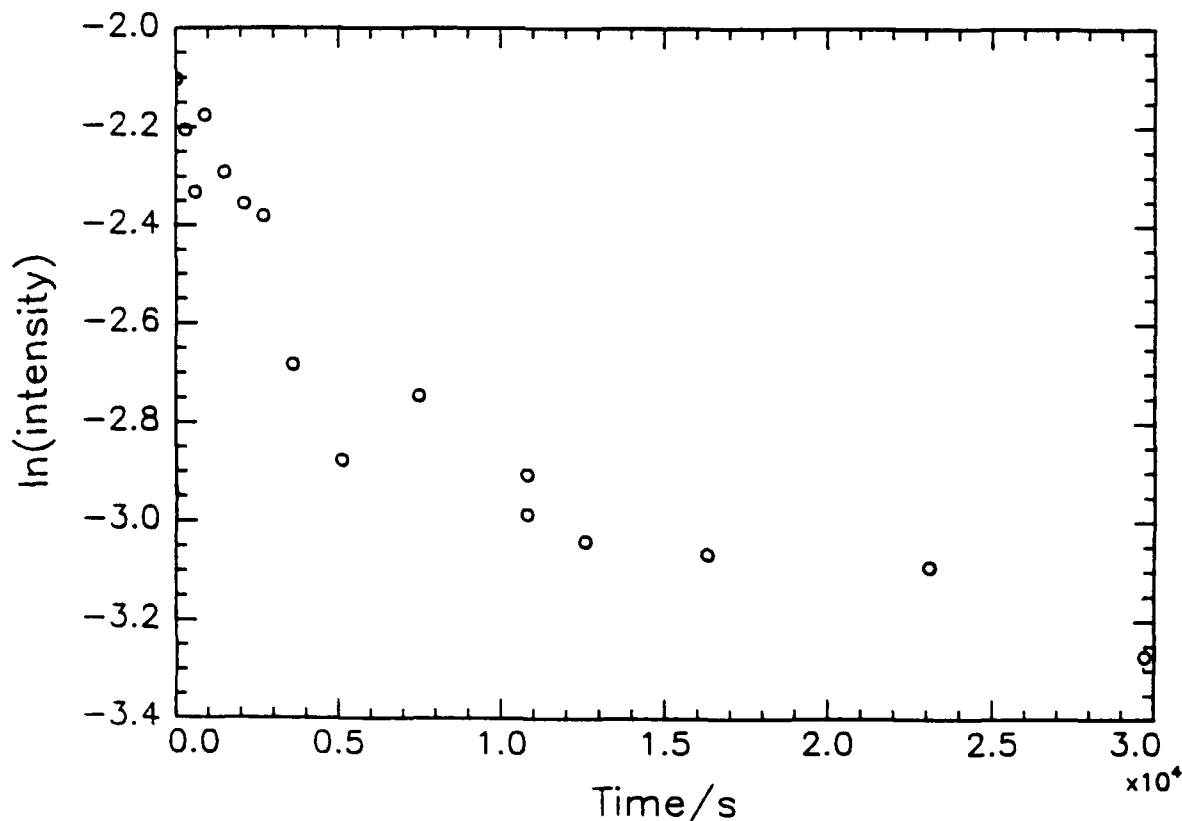
**Fig. 4.** Cross-sectional TEM image of a Ni/NiP<sub>x</sub> multilayer with a repeat length of 60 Å.

Some of the Ni crystals show Moiré fringe contrast (fine fringes) while others are not visible because they are not in the diffracting condition. The amorphous layers are thinner and uniform grey in contrast. From Ref. 12



**Fig. 5. Stress in  $\text{NiP}_x$  on Si as a function of time during annealing.**

Each scan takes approximately 90 sec. During the first 8 scans the sample was heated and the average temperature during the scan is indicated. When the sample had reached  $250^\circ\text{C}$  it was held at that temperature. Up to  $200^\circ\text{C}$  the initial tensile stress is reduced by thermal mismatch, but above that it begins to increase as densification occurs. When densification is complete, the high tensile stress relaxes by viscous flow.



**Fig. 6. X-ray peak intensity for an amorphous multilayer as a function of annealing time at  $120^\circ\text{C}$ .** The gradient of the fit through the points is proportional to the diffusivity, and decreases with time.

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# Direct Recoil Spectroscopy for Process Control During Low Pressure (< 1 Torr) Deposition

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Time of Flight (TOF) Low Energy Ion Scattering<sup>1</sup> and Direct Recoil Spectroscopy<sup>1-2</sup> using 5-15 keV Na(Ne) or K(Ar) primary ions allows quantitative identification of H, D, Li, B, C, N, O, and F on a metal or insulating surface. The experiment is performed by impinging the pulsed primary ion beam at grazing incidence and measuring the TOF of the directly recoiled surface atoms into a line of sight detector positioned at a forward scattering angle of typically 30 degrees. The resulting TOF spectrum gives a 1 amu resolution mass spectrum of the first and second row elements if present. The direct recoils have kinetic energies in excess of 1 keV and thus need not be ionized in order to be detected with near unit efficiency by a channelplate multiplier. The time necessary to obtain surface concentrations with a +/-5% precision is under one second. Furthermore, because only neutrals need be detected, DRS can be performed at pressures of up to 1 Torr in a differentially pumped reaction chamber. Similar arguments apply to measuring the TOF of the scattered primary ion/neutrals into a backscattering angle (eg., 90 degrees). Ion backscattering gives the heavier element surface composition. Both experiments can be performed simultaneously giving a complementary and complete surface analysis at moderate pressure.

The applicability of DRS for monitoring low pressure growth processes has recently been demonstrated<sup>3</sup> by measuring the average hydrogen/deuterium surface concentration as a function of substrate temperature during hot filament assisted diamond growth with 0.2 Torr CD<sub>4</sub> and 1 Torr D<sub>2</sub>. Because these results are now mostly in the literature,<sup>3</sup> this talk will focus on results obtained during boron nitride thin film growth.<sup>4</sup> Examples of spectra obtained from other compound surfaces, such as GaAs and 123 superconductors, will be briefly discussed to illustrate the general applicability of the techniques.

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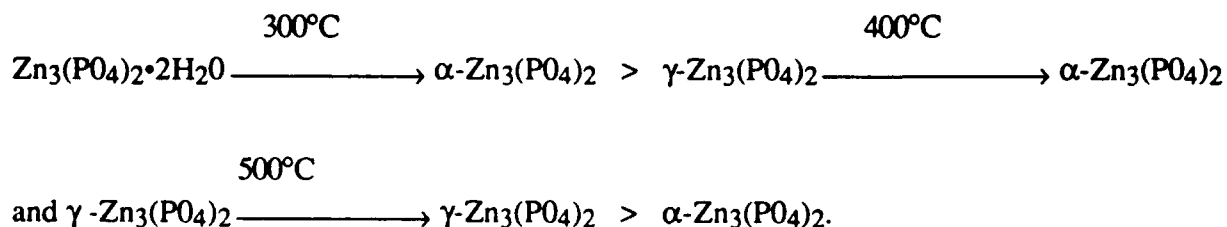
# Polyacid-Zinc Phosphate Anhydride Conversion Coatings

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In an attempt to develop the poly(acrylic) acid, [p(AA)],-modified zinc phosphate (Zn•Ph) anhydride conversion coatings suitable for use with high-temperature polymers, such as polyphenylene sulfide, polyimide, and polybenzimidazole topcoats, the characteristics of the hydrated- and dehydrated-crystal phases in the p(AA)-Zn•Ph coating systems deposited by immersing the steel in transition Co, Ni, and Mn cations, and p(AA)-incorporated zinc phosphate solutions were investigated.

With regard to the Zn•Ph hydrate phases, the control solution in the absence of transition metal additives conducts a single  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  crystal to the steel surfaces at 80°C. The dissolution of a certain amount of Co, Ni, and Mn nitrate hydrates in the control solution led to the preferential precipitation of a hopeite,  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , phase, instead of the formations of  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . One of the characteristics for the transition metal-absorbed hopeite layers was that the electron trapping behavior of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions serves in inhibiting the cathodic half reaction in term of the oxygen reduction reaction,  $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- = 2\text{OH}^-$ , during the corrosion of steel. This reflected directly to the extended lifetime of the Zn•Ph which provides corrosion protection to steel.

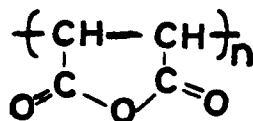
It was found that the interfacial disbandment and separation of high-temperature polymer topcoats from the hydrated Zn•Ph surfaces not only associate with the dehydration process of Zn•Ph crystal brought about by the high-temperature treatment of topcoat systems, but also is due to the alkali-induced dissolution of Zn•Ph caused by the attack of the hydroxyl ions generated by cathodic reaction. To solve these problems, attention was paid to the phase transitions of Zn•Ph at temperatures up to 500°C, and the surface chemical natures and the magnitude of susceptibility to alkaline dissolution of the dehydrated Zn•Ph. The resultant kinetics for the thermal dehydration of  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  derived from the control solution were related to the following phase transition;



In contrast, all hopeite layers, with the exception of Ni-derived hopeite, were converted into the  $\gamma\text{-Zn}_3(\text{PO}_4)_2$  anhydride as the major phase at 300°C. An estimation of alkali dissolution for these anhydride phases was carried out by comparing the rates of phosphorous dissociation from

the crystal layers after exposure to 0.1 M NaOH solution. As a result, the susceptibility of  $\alpha$ - $\text{Zn}_3(\text{PO}_4)_2$  phase to alkali dissolution was considerably lower than that of  $\gamma$ -anhydride phase.

On the other hand, the p(AA) macromolecule existing at the outermost surface sites of the Zn-Ph layer were transformed into the polyacid anhydride, (PA), macromolecule containing a ring structure,  $\left( \text{CH}-\text{CH} \right)_n$ , at 300°C. This acid anhydride group formed by the intermolecular



dehydration condensation of p(AA) favorably reacted with the high-temperature polymers. Therefore, the PA-incorporated  $\alpha$ - $\text{Zn}_3(\text{PO}_4)_2$  anhydride conversion coatings having the two important characteristics (a great resistance in alkaline solution and a good adherent property to organic topcoats) contributed significantly to the decrease in the rate of cathodic delamination of polymers from the  $\alpha$ -phase steel substrates, thereby resulting in the improvements of corrosion protection to steels at an elevated temperature.

# Atomically Resolved Imaging of Surfaces by Scanning Tunneling Microscopy

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The success of scanning tunneling microscopy (STM), first developed by Binnig, Rohrer and coworkers in 1982, in obtaining three-dimensional and atomically resolved images in real space has inspired worldwide research activities in applications of STM and improvements of the STM technique itself. In the former category, various reconstructions, phases and defects on semiconductor and metal surfaces have been extensively investigated. Ceramic surfaces, on the other hand, have been largely ignored. As an attempt to apply STM on ceramics surfaces, we present in this report images of nitrogen-doped single crystalline  $\beta$ -SiC surfaces grown on substrates of Si(001) and  $\alpha$ -SiC{0001} by the method of chemical vapor deposition (CVD).

As a structural ceramic, SiC is of value from the standpoint of its mechanical properties, i.e., high fracture strength and abrasion resistance. Pure SiC is effectively an insulator at room temperature (2.4 eV band gap); whereas SiC with nitrogen dopant levels on the order of  $10^{18}/\text{cm}^3$  is an excellent n-type semiconductor, thus making STM studies feasible. Because of its high electron mobility,  $\sim 10^3 \text{ cm}^2/\text{Vs}$ , and its thermal stability, semiconducting SiC is a promising candidate for high temperature electronic devices.

We used STM to study cubic  $\beta$ -SiC(001) and (111) surfaces. The  $\beta$ -SiC(001) surfaces were grown on Si(001) substrates, while the (111) surfaces were grown on hexagonal  $\alpha$ -SiC{0001} substrates. Atomically resolved images of the  $c(2 \times 2)$  and  $(3 \times 2)$  reconstructions of the  $\beta$ -SiC(001) surface and a  $(6 \times 6)$  honeycomb reconstruction of the  $\beta$ -SiC(111) surface are presented. The difference between the  $\beta$ -SiC(111) surfaces grown on the Si-terminated  $\alpha$ -SiC(0001) and C-terminated  $\alpha$ -SiC(0001) substrates are examined. Spectroscopic I-V measurements with the STM were also carried out on the  $\beta$ -SiC(111) surfaces to obtain information on the electronic structure of the surfaces on an atomic scale.



# Hydrogen Permeation and Positron Annihilation Study of Alpha Iron Crystals

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Michigan Technological University  
Houghton, Michigan*

Dislocation densities in deformed iron single crystals were determined by positron annihilation techniques. Electrochemical measurements of hydrogen diffusion were made on the same crystals. It was shown that apparent diffusivity  $D_0$  was inversely proportional to the dislocation density- results cover three different modes of deformation. Mechanical polishing of annealed specimens with even fine abrasives introduced sufficient dislocations to reduce the diffusivity tenfold.

Cathodic deposition of hydrogen and of deuterium atoms followed by rapid removal by potential reversal was studied on similar crystals. Holdup of the hydrogen atoms in surface layers was increased by the dislocations. The effect was stronger with deuterium charging. Surface coverage was approximately 5% of available sites.

# **Ion Beam Analysis of Surfaces and Coatings**

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and  
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Rutherford backscattering spectrometry (RBS) has become a standard technique for surface analysis of thin films. Although a powerful tool, it has limitations such as mass resolution at high target masses, poor depth resolution and ineffectiveness in detecting light elements in a heavy matrix. A host of techniques are available which are based on conventional backscattering analysis but improve in various aspects. They include high energy backscattering and nuclear resonance scattering for improved detection sensitivity of light elements, heavy ion backscattering spectrometry (HIRBS) for improved energy separation and depth resolution, and time of flight RBS (TOFRBS) for improved mass and depth resolution. In conjunction with techniques such as nuclear reaction analysis (NRA), particle induced x-ray analysis (PIXE) and elastic recoil detection (ERD), accelerator-based techniques are spanning an ever-increasing breadth of applications in the analysis of thin films. Combined with their inherent non-destructive analysis feature, they are often among the most attractive where sample supply is limited or costly.

Many of these techniques have been applied to the analysis of thin films or coatings formed by ion implantation, mixing or deposition. For example, the determination of the stoichiometry and thickness of a TiN coating formed by ion beam assisted deposition is a classic problem which can best be determined using nuclear reaction analysis. The uptake of hydrogen in the formation of diamond-like coatings can be quantitatively determined by forward recoil detection. The characterization of multilayered surface structures and the homogenization by subsequent ion beam mixing can be assessed quantitatively using conventional RBS or nuclear reaction analysis. Several examples of surface film formation by ion beam techniques and the analysis of these surfaces will be presented to highlight the capabilities of ion beam processing and analysis.

# First Principle Calculations of the Properties of Clusters and New Materials?

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Department of Chemistry  
University of California, San Diego  
San Diego, California*

Major advances in our ability to interpret materials via theoretical simulations of their structures and dynamics have been made possible by the appearance of ultra-fast computers. In this talk I will discuss these approaches emphasizing methods that are based on the local density approximation (LDA) to the many electron Schrödinger equation. The LDA equations provide predictions with sufficient accuracy such that important conclusions may be drawn for very complex systems. They can be implemented very efficiently on advanced vector and parallel computers. Algorithms are now so rapid that the dynamics of chemically complex materials can be simulated for reasonably long times. This has important implications both for structural and dynamical studies since, for very complex materials, the prediction of structure may require an extensive search of possible configurations which can now be done by dynamical simulation.

The key point is that in these approaches the interactions between atoms in the system are calculated from first principles. Traditional simulation approaches require bonding information in the form of phenomenological forces between the atoms (e.g., harmonic forces, Lennard-Jones equations, etc.). These equations require parameterization from experimental or theoretical data. In cases where predicted results have been compared to known structures, such phenomenological methods have been shown to have very limited reliability.<sup>1</sup>

In this talk the approaches that we and others have implemented will be discussed in the context of our calculations of the properties of metal and semimetal clusters. These materials are a challenge to simulate, because the character of their bonding changes dramatically in going from the small molecule to the bulk limit. While it is known that their properties are a strong function of cluster size, for example, the reactivity of boron clusters changes by orders of magnitude in going from 12 to 13 atoms. The reasons for these changes are unknown. Now we can study them within a first principle theory. Our results provide detailed information about the growth of simple metals and semimetals. The growth pattern is very different from that previously proposed and very different from structures obtained from force modeling approaches. Remarkably, for the Be system, bulk-like structures appear for sizes as small as 11 atoms.<sup>2</sup> For the semimetal boron, on the other hand, the minimum energy structures for small systems appear to be quite different from those of the bulk. For example, the 12 atom minimum energy configuration is not an icosahedron. However, it can be related to icosahedral units of the bulk by recognizing the importance of dangling bonds in determining structure.<sup>3</sup>

The limitations of first principle approaches will also be discussed. At present their application is limited to systems which would be considered to be complex to condensed matter physicists, but would still be simple on the scale of some of the systems discussed in this meeting. On the other hand, the approaches scale well with size. With the rapid growth of computational speed, much more complex systems will be treated in the next few years.

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## Characterization of Protective Films on Steel and Metal Matrix Composites

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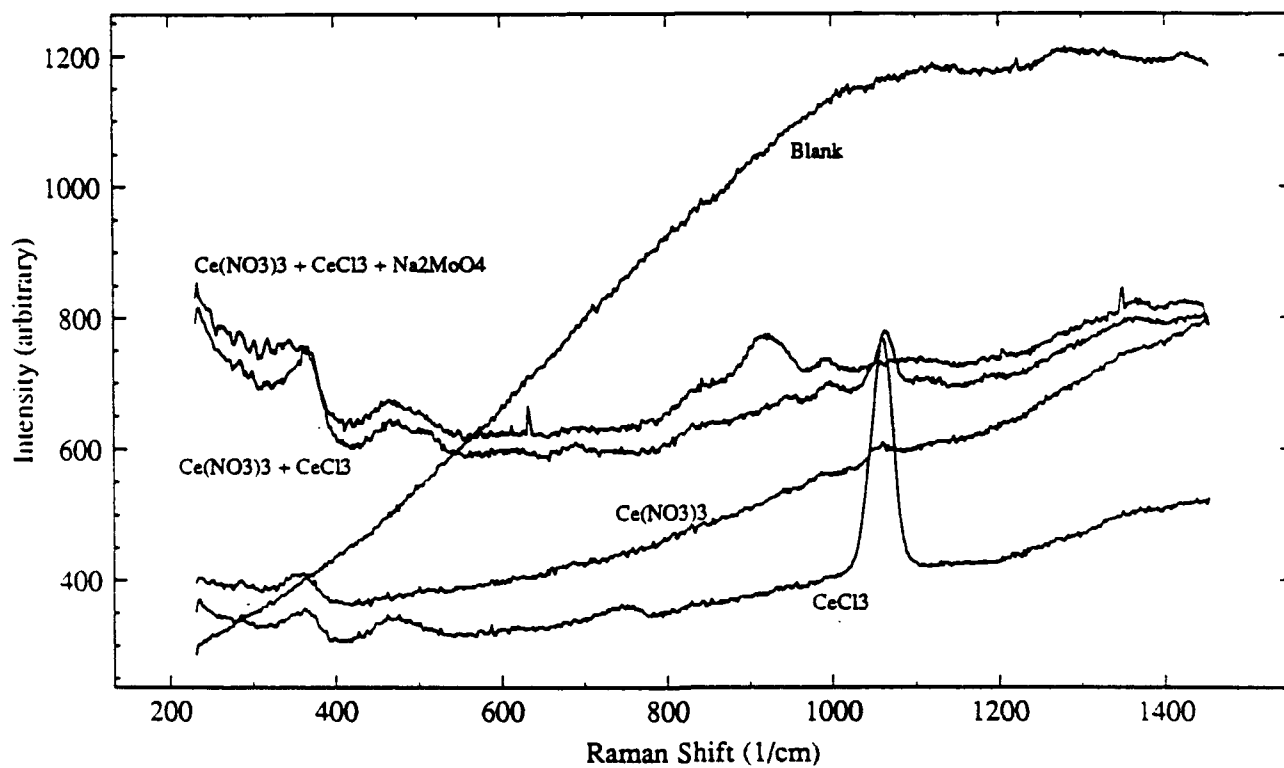
This cooperative project is aimed at furthering our understanding of the formation and performance of certain protective films by applying Raman spectroscopy, tunable diode laser infrared reflection-absorption spectroscopy (IRRAS), scanning tunneling microscopy (STM), atomic force microscopy (AFM), and electrochemical impedance spectroscopy (EIS). The films are polymer modified zinc phosphate (Zn:Ph) based protective coatings on steel, protective films formed on Al and Al-based metal matrix composite (MMC) materials formed by immersion in rare earth chloride solutions, and passive films formed on iron in aqueous solutions. The Zn:Ph film study is in collaboration with T. Sugama at BNL; the MMC studies are in collaboration with F. Mansfeld at USC. Two other thin film systems have presented themselves which are also of immediate technological interest. They are plasma deposited carbon polymer films (in collaboration with C. Yasuda, MU) which are useful due to their chemical and mechanical properties, and the conducting polymer polyaniline (with D. Cowan, MU).

**Zn:Ph coatings**—Analysis of early samples with Raman had shown no support for Sugama's three layer model of the Zn:Ph coated surface. Subsequent samples prepared with pure iron substrates showed clear presence of species other than Zn:Ph. However, these other species are not in a simple layered structure; they are more island-like. We are in the process of identifying these species by collecting reference spectra for likely candidates. Classical STM of poly(acrylic acid) did not successfully resolve the molecule.

**Ce coatings**—Raman spectra, shown in Fig. 1, on a recent series of Al samples coated at USC with various protective films show features peculiar to the chemical composition of the treatment bath. The baths contain mixtures of rare earth chlorides and nitrates with various treatment times and temperatures. Earlier we had obtained Raman spectra on samples of 6061-T6 soaked in various rare earth chloride solutions in an attempt to identify the characteristic signatures of the rare earth and chloride ion in the protective film. We are now trying to correlate spectral features with film composition and morphology in the recent series of samples.

This work has been supported by the U.S. Army Research Office under Contract No. DAAL03-89-K-0084.

# Aluminum 6061-T6



**Fig. 1. Raman spectra of Al 6061-T6 samples prepared by the USC group.**

<u>Label</u>	<u>Treatment</u>
Blank.....	None
CeCl <sub>3</sub> .....	5mM CeCl <sub>3</sub> at elevated temperature
Ce(NO <sub>3</sub> ) <sub>3</sub> .....	10mM Ce(NO <sub>3</sub> ) <sub>3</sub> at elevated temperature
Ce(NO <sub>3</sub> ) <sub>3</sub> + CeCl <sub>3</sub> .....	10mM Ce(NO <sub>3</sub> ) <sub>3</sub> at elevated temperature ..... then 5mM CeCl <sub>3</sub> at elevated temperature
Ce(NO <sub>3</sub> ) <sub>3</sub> + CeCl <sub>3</sub> + Na <sub>2</sub> MoO <sub>4</sub> .....	10mM Ce(NO <sub>3</sub> ) <sub>3</sub> at elevated temperature ..... then 5mM CeCl <sub>3</sub> at elevated temperature ..... Then polarized in 0.1M Na <sub>2</sub> MoO <sub>4</sub> under + 500mV ..... (SCE) at room temperature

# ***Poster Session***

## ***ABSTRACTS***

*for the*

*The University of Michigan*

*&*

*Army Research Office*

*Workshop on:*

***SURFACE SCIENCE & TECHNOLOGY***

## **Phase Separation in Growing Films**

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We present both experimental results and analytical theory on the nature of phase separation during the vapor phase growth of films. The phase and grain microstructure and surface morphology of Al-Ge films formed by electron beam co-deposition have been studied as a function of deposition temperature. X-ray diffraction, scanning and transmission electron microscopy with x-ray fluorescence analysis were used to characterize the films. At room temperature and above, crystalline, phase separated films are obtained. The phase dimensions and surface roughness were observed to increase with the deposition temperature and dependence yields activation energy for atomic migration consistent with a surface diffusion mechanism. The surface roughness is observed to reflect the microstructure under the surface.

Based upon these results, a theoretical analysis of phase separation in growing films was developed which focuses on surface diffusion control. This analysis is based upon the derivation of a surface diffusion equation which accounts for a finite deposition rate of arbitrary composition and the finite deposition rate. Spinodal decomposition, lamellar growth and Ostwald ripening are all analyzed for the co-deposited film growth geometry. The theoretical results are then compared with the experimental data described above.



## **Deposition of Improved Ordnance Coatings**

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An important part of the Benet Laboratories' effort is to develop new and improved methods for producing erosion and wear resistant coatings. Several projects are focused on (1) upgrading the state-of-the-art in chromium electrodeposition to produce adherent deposits containing minimal structural defects and residual strains and (2) developing and evaluating other promising processes such as molten salts and high rate sputtering to deposit various refractory metals, alloys and ceramic coatings which are able to withstand applications requiring very high temperatures and pressures.

The approach taken in these efforts is to develop an understanding for the deposition techniques and to establish the relationships between deposition process parameters and the physical and mechanical properties of the coatings.

Accompanying the experimental work, a metallurgical analysis that examines the morphology, structure, and property relationships is used to evaluate the influence of the process parameters on the quality improvement of the resulting deposits. The coatings developed along with optimization techniques are presented and some potential advantages and enhancements are discussed.

In addition to the thrust in research and development of coatings, Benet has transitioned and implemented full-scale production facilities for application of advanced coating materials to ordnance components.

# **Oxide Formation and Anodic Polarization Behavior of Thin Films of Amorphous and Crystalline Fe-Cr-P Alloys Prepared by Ion Beam Mixing**

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An experimental program has been conducted to determine the effect of phosphorus on the corrosion and passivation behavior of Fe-Cr-P alloys. Chemically homogeneous 60 nm films of Fe-10Cr-xP (x from 0 to 30 at%) on polished Fe-10Cr substrates were prepared by multilayer evaporation of iron, chromium, and iron phosphide, followed by ion beam mixing with 300 keV Kr<sup>+</sup> ions to a dose of  $5 \times 10^{15}$  i/cm<sup>2</sup> at a temperature of -100°C. The structure and composition of the films were confirmed by TEM, XEDS, and RBS. Films with a phosphorus content greater than approximately 20 at% were found to be entirely amorphous, while films with smaller phosphorus contents consisted of both amorphous and bcc phases. Recrystallization of the amorphous phase was accomplished by heating the samples to 350°C in a purified argon flow furnace for 6 hours.

Anodic polarization of the alloys in 0.1N sulfuric acid has shown the Fe-10Cr-xP films to be more corrosion-resistant than Fe-10Cr, with a smaller dissolution rate in both the active and passive potential regions. There is a direct relationship between the amount of phosphorus in the film and the corrosion resistance, with maximum resistance at a phosphorus level sufficient to completely amorphize the film. Surprisingly, even greater corrosion resistance is observed when the amorphous films are recrystallized by heat treating. All of the passive oxides were examined by XPS and depth-profiled by argon sputtering. Phosphorus appears to enhance passivation by forming a phosphate film between the ordinary Fe-Cr oxide and the underlying metal.

## **Coefficients of Friction of Ion-Implanted Alumina Using a Low Load, Low Velocity, Single Pass Device**

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Polycrystalline alumina cylinders (99.8+% pure and 0.500 " high x 0.250" in dia.) were faced with a 320 grit diamond sectioning saw and ground with 600 grit carbide paper. When nominal RMS roughnesses of 0.22-0.25 microns were attained, cylinders were set aside from which matched sets were later chosen. The opposing material in this couple was a stabilized beta-titanium alloy (composition, wt. %: 79Ti, 11Mo, 6Zr, and 4Sn). These rectangular wires (0.017" x 0.025") were evaluated in the as-received state in which optical RMS roughness measurements were found to equal 0.14 microns. In addition, two ion-implanted couples were evaluated: one in which Ti<sup>+</sup> was implanted into the alumina but the alloy remained unchanged, and another in which the Ti<sup>+</sup> implantation of the alumina was opposed by a N<sup>+</sup> implantation of the beta-titanium alloy. In both cases, specimens were subjected to multiple implantations (five) in a Varian 350D ion implanter. The coefficients of friction ( $\mu^s$  and  $\mu^k$ ) were measured by a double contact friction device. The flats on the alumina cylinders were drawn past the 5" long beta-titanium wire at a rate of 1.0 cm/min under prevailing atmospheric conditions. The slopes of the regression lines of frictional force (f) vs. normal force (nominally, N = 0.2 to 1.0 kgs) yielded the values of  $\mu^s$  and  $\mu^k$ .

Plots of f vs. N showed that the static and kinetic coefficients of friction displayed a linear behavior and extrapolated close to origin. Although the slopes of the control/control and the Ti<sup>+</sup>/control couples were not very different, the slopes of the Ti<sup>+</sup>/N<sup>+</sup> implantation of the alumina/beta-titanium couple were significantly different than the other couples. The mean static coefficients decreased from 0.50 (control/control) to 0.20 (Ti<sup>+</sup>/N<sup>+</sup>). Similarly the kinetic coefficients decreased from 0.44 (control/control) to 0.25 (Ti<sup>+</sup>/N<sup>+</sup>). Apparently the plowing tendency of the rough and sometimes faceted alumina surface is reduced by the hardening afforded by the N<sup>+</sup> enriched surface of the beta-titanium alloy.

## **Corrosion Protection Coatings for Depleted Uranium Alloys**

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High density depleted uranium (DU) alloys possess superior armor piercing capabilities but they are susceptible to corrosion on exposure to high humidity and salt laden environments. In order to minimize and/or eliminate corrosion, protective coatings have been applied for DU alloys either by electroplating or by physical vapor deposition method. These coatings have been characterized by electrochemical polarization tests in salt solutions and have been evaluated in cyclic temperature/humidity conditions and salt-fog atmosphere. The results indicate that sacrificial type coatings are very effective in preventing DU corrosion. Potential use of these coatings for armament applications are indicated.

## **Assessment of Some Corrosion Protection Schemes for Magnesium Alloy ZE41A-T5**

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U.S. Army experience with magnesium alloys as components in aircraft has shown a significant corrosion problem requiring increased maintenance and impacting both cost and readiness. During the Vietnam era there was widespread use of magnesium in Army aircraft to reduce weight and increase performance. But in a recent modernization program, a number of magnesium parts have been replaced with aluminum to reduce the corrosion problem. It is clear that more corrosion-resistant magnesium alloys with improved protective schemes are needed before their advantages can be fully utilized.

The best current practice for protecting magnesium in Army aircraft employs an anodize or chromate conversion treatment, an epoxy primer and a polyurethane topcoat. This paper assesses a protective scheme for Mg alloy ZE41A which has been modified by the British approach of interposing a baked epoxy resin (sealer) between the conversion coating and primer application. For comparison, the current practice described above is also assessed.

Magnesium alloy ZE41A-T5 was selected because it is presently being used in our newest aircraft. The nominal composition of this alloy, the heat treatment and mechanical properties are:

Nominal Composition	Zinc	3.5-5.0%
	Rare Earths (Ce)	1.2%
	Zirconium	0.4-1.0%
	Magnesium	balance
Heat Treatment	625°C (2 hrs), Air Cool	
	340°C (10-16 hrs), Air Cool	
Mechanical Properties	Tensile Strength	28.0 Ksi
	Y.S. (0.2% offset)	19.5 Ksi
	Elongation	2.5%
Corrosion Resistance	Immersion for 28 days in 3% NaCl	120 mpy
	Salt Spray	600 mpy
	Polarization: 100 ppm Cl NaCl	7 mpy
	3.5% NaCl	115 mpy

The corrosion resistance in mpy obtained by both immersion in 3% NaCl solution and electrochemical polarization in both 100 ppm Cl and 3.5% NaCl solutions is also included. Note that the immersion and polarization data in 3.5% NaCl solution are in good agreement, 120 and

115 mpy, respectively. The protective schemes evaluated included the initial conversion coating (HAE anodize [MIL-M-45202C; 1A2] or Chrome-Manganese [DTD911C; Bath V]), the presence of the sealer (Araldite 985 [D.T.D. 935]) and the primers (1. Epoxy Polyamide, CSR [MIL-P-23377], 2. Epoxy Resin, CR, [MIL-P-52192], 3. Epoxy, VOC Compliant, CSR [MIL-P-85582]). The chemical agent resistant polyurethane topcoat was standard for all systems evaluated.

The testing program included exposure to both salt spray (fog) and 100% humidity. Tape adhesion tests were performed after exposure to 100% humidity. In addition to the above, electrochemical AC impedance measurements were carried out to evaluate the performance of the coating/metal systems. AC impedance was performed with a PARC 273 potentiostat in conjunction with a PARC 5208 Lock-In Amplifier, Apple II computer, and the PARC Softcorr 368 program. Measurements were obtained at the corrosion potential over the frequency range 100K Hz - 0.01 HZ for up to 42 days in 100 ppm Cl solution. The corrosion potential was monitored before each experiment.

The results were: (1) The salt spray resistance of the MIL-P-23377 primer was not as good as either the MIL-P-52192 or MIL-P-85582 primers regardless of the initial treatment (CrMn or HAE anodize). (2) The application of the Araldite 985 sealer significantly improved the performance of the MIL-P-23377 primer particularly when the HAE anodize was used. (3) The AC impedance data also demonstrated the beneficial effect of the sealer in conjunction with the HAE anodize. (4) The Araldite sealer also contributed significantly to improving the salt spray resistance of the polyurethane CARC MIL-C-46186 topcoat regardless of the primer used and the initial treatment. (5) Despite the beneficial effect of the sealer in salt spray resistance of the primers, tape adhesion tests showed that the adhesion of the primer to the sealer was poor after 5 weeks of exposure to 100% relative humidity. As a consequence, efforts are now underway to improve the adhesion of sealer to primer by employing a post baking treatment. Also, other sealers are being investigated. (6) The AC impedance data appeared to provide an estimate of the film integrity and protective capability of the primers which correlated with the salt spray test results. Values of polarization resistance below  $10^6$  ohm-cm<sup>2</sup> indicated significant degradation.

# **The U.S. Army's Present and Future Coating Needs and Problems for Fasteners for Military Vehicles**

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Thousands of fasteners, bolts, nuts and washers are used in the manufacturing of all military vehicles. The coating applied to the surfaces of these fasteners for corrosion protection and uniformity of assembly are as important as the composition of the steel.

**Background:** Cadmium plating has been the predominant coating requirement for military fasteners for many years. It easily meets the minimum salt spray requirements for corrosion protection. Torque requirement charts in the technical manuals (TM) for military vehicles are based on the surface characteristics of cadmium plated fasteners.

**Present Status and Problems:** The following environmental factors have reduced the availability of cadmium plating facilities for economic and health reasons:

1. Cadmium has been placed on the list of hazardous materials in the USA.
2. In February, 1990, OSHA issued a proposed occupational standard that will have a serious impact on the use of cadmium. This standard may become effective within 6 to 12 months.
3. The Army Material Command (AMC) has directed use of zinc for plating of fasteners in lieu of cadmium.
4. Prime contractors and U.S. Army Commands oppose this change for fasteners with class-3 fit requirements and some electrical applications.
5. The use of cadmium has been banned in Europe because of toxicity.

**Present and Future Needs:** Zinc plating is less expensive than cadmium plating but has some shortcomings. Its corrosion protection properties and surface characteristics are less desirable for fastener coatings.

Therefore, the U.S. Army needs a substitute coating that will be economically feasible to use on fasteners, will provide corrosion protection equivalent to cadmium, and will have surface characteristics suitable for uniform assembly.

## **Molecular Organization of Poly(imides) Near Surfaces**

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Details of the molecular organization occurring during imidization of the poly(amic acid) PMDA-12C at temperatures below the bulk melting point were examined. In particular, the effects of surface constraints were investigated by studying structural evolution in thin droplets. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) experiments on as-cast and imidized droplets illustrated the development of surface roughness and fluctuations in mass thickness. High Resolution Electron Microscopy (HREM) studies near the droplet edge showed discrete crystallites containing uniformly spaced 1.8 nm (001) fringes which correspond to the repeat distance along the polymer backbone. The crystallites were found to be slightly extended in the axial direction, with an average axial dimension of  $53 \pm 23$  nm, and average lateral size of  $38 \pm 13$  nm. The polymer chains within 100 nm of the droplet edge were oriented both in the plane of the droplet and parallel to the droplet edge. Certain crystallites appeared to contain internal bending deformation (with the radius of curvature as small as 50 nm). Evidence for different types of grain boundaries between adjacent crystallites was obtained. Based on these observations, the molecular structure of these interfaces and their possible influence on the physical properties of crystallizable polymers are discussed.



## **Evaluation of Solid Lubricants: A Surface Analytical Study of MoS<sub>x</sub> Films**

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The surface chemistry of molybdenum disulfide (MoS<sub>2</sub>) lubricating films has been investigated using Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), and Thermal Desorption Spectroscopy (TDS). These techniques have also been used to evaluate the effect of nitrogen ion beam modification of MoS<sub>2</sub> solid lubricant films. The MoS<sub>2</sub> lubricant films were deposited on molybdenum foil substrates using radio-frequency sputtering and burnishing techniques. Surface analyses were performed at temperatures ranging from ambient to 900K in an effort to investigate the effect of oxidative degradation of MoS<sub>2</sub> solid lubricant films. The surface chemical analyses will show that the degraded lubricating films are oxidized to form MoO<sub>3</sub> and that the extent of oxidation can be greatly reduced with the aid of ion beam modification techniques. The results will also show that these investigational techniques can provide information for critical *in-situ* assessment of the capability and operational limits of solid lubricant systems.

# **Influence of Cyclic Deformation on Surface Microstructure and Hardness of Ion-Implanted Nickel**

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The effects of cyclic deformation on near-surface dislocation structure and hardness of ion-implanted nickel were characterized and correlated with the evolution of fatigue damage. Polycrystalline nickel fatigue specimens were self-implanted at 220°C with 350 keV and 3 MeV nickel ions to a fluence of  $1 \times 10^{16}$  ions/cm<sup>2</sup> and aluminum-implanted at 220°C and 500°C with 350 keV aluminum ions to a fluence of  $5 \times 10^{17}$  ions/cm<sup>2</sup>. Both the self-implantations and aluminum-implantations approximately doubled the hardness of the near-surface region. During cyclic deformation, the near-surface regions of self-implanted specimens cyclically softened and formed clear channels through which subsurface persistent slip bands (psbs) penetrated the implanted region. The near-surface regions of aluminum-implanted specimens maintained a high surface hardness during cyclic deformation and effectively suppressed the evolution of fatigue damage and extended fatigue life. The results of the study indicate that the cyclic stability of implantation-induced surface hardening is a key factor in the ability of an ion implantation treatment to suppress the evolution of fatigue damage.

# **A Study of the Deposition and Electrochemical Properties of Ruthenium-Titanium Oxide Thin Films**

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Ruthenium-titanium-oxide thin films have been produced on niobium and glass substrates using a plasma-assisted reactive ion plating process. Structure-chemistry-electrochemical property relationships for these materials have been studied using a range of microanalytical techniques (SEM, TEM, Auger, etc.) and anodic polarization techniques. A relationship was found between the oxygen flow and metal evaporation rates and the resulting film microstructure, chemistry, and crystal phases. Solid solutions of ruthenium in  $\text{TiO}_2$  (rutile) and  $\text{TiO}$  (cubic) formed at average oxygen flow rates below 95 sccm. Films with a dual phase mixture of  $\text{RuO}_2$  and  $\text{TiO}_2$  (rutile) were produced when average oxygen flow rates were equal to or exceeded 95 sccm. The presence of  $\text{TiO}_2$  (anatase), with  $\text{TiO}_2$  (rutile) and  $\text{RuO}_2$ , was shown to be related to a lowering of the ruthenium evaporation rate and a corresponding decrease in overall ruthenium (and  $\text{RuO}_2$ ) content. Films comprised of 80-90 at.% titanium (20-10 at.% ruthenium) in the form of a dual phase mixture of  $\text{RuO}_2$  and  $\text{TiO}_2$  (rutile) exhibited the greatest degree of electrochemical activity of those films fabricated and tested for the study, i.e., they possessed the ability to maintain a stable flow of current with little or no rise in applied potential for extended periods of time. Electrochemical activity was diminished in those ruthenium-titanium-oxide films containing either  $\text{TiO}_2$  (anatase) with  $\text{TiO}_2$  (rutile) and  $\text{RuO}_2$ , or ruthenium in solid solution with  $\text{TiO}_2$  (rutile) or  $\text{TiO}$  (cubic). There is evidence suggesting the possibility that a  $\text{TiO}_2$  (rutile)-to- $\text{TiO}_2$  (anatase) phase transformation is induced by anodic polarization in films containing both  $\text{TiO}_2$  (anatase) and  $\text{TiO}_2$  (rutile). It is also suggested that an amount exceeding 5 at.% ruthenium is required to stabilize the rutile form of  $\text{TiO}_2$  in films comprised of  $\text{RuO}_2$  and  $\text{TiO}_2$ . The study shows that a combination of ruthenium depletion and substrate oxidation are mechanisms by which the oxide films on niobium lose their electrochemical activity under anodic polarization.

## **Thermal Wave Surface Characterization and Modification**

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The photoacoustic or thermal wave technique offers a unique path for evaluation of the surface and near surface thermal properties and structure of a material. An example of one micron surface resolution will demonstrate the detail available. The variety of detection approaches will be illustrated with gas cell images, photoinductive images showing resolution 15 times better than achieved before with an eddy current imaging approach and an image generated by an ion beam in which piezoelectric detection was used. Work in progress relating gas cell images obtained with high laser intensity, which intentionally modified the surface, to subsequent x-ray measurement of residual stress will be presented. The status of work in quantifying the thickness and thermal properties of chemical vapor deposited silicon carbide coatings will be reviewed.

## **Surface Modification of Fibrous Ballistic Materials**

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It has long been speculated that the ballistic performance of woven materials may be affected by the inter fiber friction in the weave. However, no data base exists which relates fiber frictional properties to ballistic resistance of the woven fibers.

The work discussed in this poster presentation will review recent results of preliminary friction testing of poly(olefin) fibers. We have established that the frictional character of poly(propylene) fibers of different tenacities can be varied in a crude way through topical treatments such as scouring, water repellant finishes and permanent press treatments. A more interesting fiber with respect to ballistic resistance, gel-spun poly(ethylene), has also been shown to develop varying surface friction coefficients with topical treatments.

Also discussed in this poster are preliminary ballistic testing results and surface grafting chemistry. The chemistry described is a more refined surface treatment than topical treatments and has been conducted by UV reactions on poly(propylene) and poly(ethylene) film surfaces as model reactions for the final application: fiber surface grafting for low weight frictional coatings.

# **Advanced High Temperature Diesel Engine Technology Research Needs**

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Advanced high temperature diesel engine designs continue to be pursued by the Army. Thick ceramic coatings (greater than .050 inch, plasma sprayed zirconia) are being considered for piston dome, head combustion face and upper liner regions. Monolithic ceramics are being employed in valve seat, exhaust port and turbocharger turbine wheel designs. Of great importance is the development of high temperature tribology systems which include capable synthetic liquid lubricants and wear-resistant ceramic coatings for piston rings and liners. Some far term designs include liquid/solid lubrication schemes. Research needs exist in all these areas. Improvements are required to provide reliable military low heat rejection engine component designs.

General research needs for improvements in ceramics/ceramic coatings are given as follows:

- Develop new materials specifically for advanced heat engines.
- Improve properties and reliability of existing materials by improving processing techniques. Minimize material flaws.
- Provide methods for depositing and bonding ceramic coatings that will not crack or spall in a severe transient engine environment.
- Understand interaction of processing techniques and effect on microstructure, microchemistry and critical material properties.
- Compile standardized material design data and conduct standardized material property tests.
- Generate life prediction modelling techniques and improve fast fracture, slow crack growth, and fatigue models.
- Develop quick, simple, non-destructive evaluation techniques.
- Provide new processing techniques for ceramic to metal joining.

In addition to ceramic research needs, the need exists for research and development of advanced high temperature tribology systems. General research needs include:

- Understand the interaction of base lubricant and additive package on contacted engine materials and the deposit forming mechanisms.
- Find better correlation between friction, wear and deposit test rig data and that of actual engine operation.
- Develop wear-resistant or self-lubricating materials to be used with high temperature capable lubricants to reduce friction and wear under borderline lubrication conditions.
- Determine a basic understanding of solid lubrication friction and wear mechanisms and identify viable schemes for far term engine application.

# **Growth of Diamond and Diamond-like Carbon Films and Characterization by Raman Scanning Electron Microscopy and X-Ray Photoelectron Spectroscopy**

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We have deposited diamond and diamond-like carbon films on Si<111> using hot filament assisted chemical vapor deposition at low pressures in the range 50mTorr-25Torr. Diamond films deposited at different relative concentrations of methane (ranging from 0.25% to 2.0%) in methane-hydrogen mixtures have been characterized by Raman spectroscopy, scanning electron microscopy and x-ray photoelectron spectroscopy. With varying methane concentration, Raman spectra show features characteristic of crystalline diamond, diamond-like carbon, and polycrystalline graphite. Films grown at 50mTorr clearly show a  $1332\text{ cm}^{-1}$  diamond peak superimposed on the Raman spectrum characteristic of diamond-like carbon. Scanning electron micrographs show densely packed diamond crystallites. SEM measurements made on diamond films grown as functions of time show that the median grain size of the diamond crystallites increases almost linearly with time during the initial phase of the growth. X-ray photoelectron spectroscopy reveals differences between the diamond  $\text{sp}^3$  covalent bonding and  $\text{sp}^2$  graphitic bonding as a function of methane concentration. The plasmon loss shoulder, characteristic of graphite, is absent from the spectrum of 0.25% methane concentration film but it appears in the XPS spectra of films grown at higher concentrations.

## **Positron Lifetime Spectroscopy in Thin Polymer Coatings**

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Polymer coatings are finding increasing applications in aerospace industry. They are being used for thermal control on aerospace structures and protective/insulating layers on optical/microelectronic components. However, the effectiveness of coatings depend strongly on their microstructure and adhesion to the substrates. Currently, there is no technique for adequately monitoring the quality of the coatings. We have adapted Positron Lifetime Spectroscopy for the investigation of thin coatings. Results of measurements on 0.001" thin polyurethane coatings on aluminum and steel substrates and thicker (0.080") self-standing polyurethane discs have been compared. In all cases, we find positron lifetime groups centered around 550 ps, corresponding to the presence of  $0.7 \text{ \AA}^3$  free volume cells. This indicates that the morphology of thin coating is similar to that of the bulk polyurethane. These results and their microstructural implications will be discussed.



## **Measurement and Evaluation of Structural Adhesive Bond Quality/Strength**

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The application of ultrasonic techniques to bondline evaluations have been shown to add significantly to a body of knowledge in helping to establish an effective tool to supplement mechanical testing of bonded joints, where thin layers of adhesives are used. The use of ultrasonic waves can significantly expedite them and reduce the volume and time of experimental testing programs. Several important properties of adhesion between an adhesive and a substrate have been studied by inducing shear deformation at a bonded interface. Bond strength is known to be dependent upon a large number of variables; and thus NDE Inspection methods must be capable of assessing such a multivariable process. Elastic properties of a material can be correlated with the strength of an adhesive bond. The use of interfacial guided waves can be used to produce shear stresses at an interface. According to the theory, the effective shear modulus of an adhesive can be calculated on the basis of its measured velocity and attenuation parameters. The effective shear modulus can be used to help characterize the effective elastic properties of a multilayered adhesive system.

In the present research, attention is being focused on an adhesively-bonded steel/adhesive/rubber interface to study the feasibility of future applications to the case/insulation bond in the Space Shuttle. Amplitude and attenuation information was obtained for a transmitted sound wave versus stress loads for several test samples. Data was compared for the good and poor bond conditions. The behavior patterns of the attenuation data for the good and poor bonds were found to be opposite in terms of the structure of the curves. For the good bond it was observed that the sample failed within (cohesive) the rubber, leaving the adhesive in tack on the mounting plate. In the case of the poor bond the failure mode was adhesive, leaving the mounting plate essentially clear of any adhesive materials.

This information will be used to help correlate bond strength of structural adhesive interfacial bonds used in critical applications of aerospace materials. Additional data will be obtained to relate both attenuation and velocity to an effective shear modulus of bonded interfaces.

## **Elastic and Capillary Failure of Films**

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When the surface and interfacial energies are such that a continuous, deposited film is unstable with respect to the formation of islands (i.e., beading up), the microstructure of the film plays a crucial role. In the present paper, we analyze the capillary mechanism by which the film fails. The film failure process generally consists of the following stages: (1) grain boundary grooving (especially at multi-grain junctions), (2) hole formation, (3) hole growth, (4) hole impingement, and (5) island formation.

Stresses in a film can lead to film failure in two distinct ways. The first is by film blistering. This process requires either a crack through the thickness of the film, debonding along the film/substrate interface, or both. A simple linear elastic fracture mechanics argument demonstrates the salient features of film blistering. The second stress-induced film failure mechanism involves the basic instability of a surface of a stressed film. We demonstrate that even when a film tends to wet a substrate based upon surface/interfacial energy criteria, the presence of stresses within the film can also lead to film failure via island formation. The size and spacing of the islands depend on the stress within the film.

## **IR Thermal Wave Imaging of Coatings<sup>†</sup>**

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We describe a recently developed type of thermal wave imaging which has excellent speed, resolution, and sensitivity for the nondestructive evaluation of coatings. We use an 8 $\mu$ m-12 $\mu$ m infrared video camera in conjunction with synchronous heating and real-time image processing. The resulting enhancement in signal-to-noise ratio, together with the capability of selectively imaging features with a given time-lag with respect to a repetitive pulsed excitation, permits thermal wave imaging of coating thickness variations and a variety of subsurface adhesion defects. We discuss its application to several coating problems, including plasma-sprayed thermal-barrier ceramic coatings on steel diesel engine pistons, and polymer coatings on metals.

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# Catalytic Oxidation Coatings for Ambient Temperature Air Purification

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An extensive research effort to develop CO-oxidation catalysts with high activity near room temperature has been in progress at the Langley Research Center of NASA for the past several years. The initial impetus for this research effort was the need to regenerate  $\text{Co}_2$  from its dissociation products, CO and  $\text{O}_2$ , in pulsed lasers. As a result of this research a new catalyst consisting of gold and manganese dioxide ( $\text{Au/MnO}_2$ ) has been developed which exhibits high activity at room temperature with virtually unmeasurable decay. Although  $\text{Au/MnO}_2$  has high activity for the stoichiometric mixtures of CO and  $\text{O}_2$  produced in  $\text{Co}_2$  lasers, its activity is significantly higher at high  $\text{O}_2$  concentrations such as that in air. Therefore, this catalyst is now being studied for possible air purification applications as well. The present paper presents results obtained to date as well as current research and future plans.

## **Thermal Diffusivity of Diamond Films**

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Among the unique physical properties of diamond films is the thermal diffusivity which is critical for its performance in many applications. The thermal shock resistance parameter of diamond films is high due to the large value of the thermal diffusivity, which leads to high threshold for laser induced damage. Similarly, it is critical to elevated temperature operation of diamond electronic devices and diamond coatings for tribological applications. Defining the limits of the applicability of diamond films requires a measurement of the thermal diffusivity of diamond films. The high thermal diffusivity and thin film geometry make standard thermal analysis inadequate for experimental determination. We have developed a laser pulse technique which is suitable for film deposited on a substrate. Polycrystalline films were deposited on a silicon substrate using a microwave plasma deposition system. The effective thermal diffusivity of diamond film on silicon was measured with a phase lag technique. An analytical model is developed to calculate the effective in-plane (face-parallel) diffusivity of a two layer system from the thermal properties of the layers. The model is used to reduce the effective thermal diffusivity of the diamond/silicon sample to a value for the thermal diffusivity and conductivity of the diamond assuming the specific heat of the diamond is known.

## **Growth and Characterization of Thin Epitaxial CoSi<sub>2</sub>(110) Films on Si(110): Anisotropic Misfit Relief**

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Single crystal epitaxial growth of CoSi<sub>2</sub>(110) on Si(110) surfaces has been observed under UHV conditions for the first time. These films are of very high epitaxial quality with  $\chi_{\min} < 4\%$ . The template methods used to grow these layers and the methods used to thicken these thin films will be presented and shown to be applicable to a wide range of ultrahigh strength high temperature materials. The strain in 30 to 150Å thick silicide films has been measured using RBS rocking curves about the [100] and [111] poles. These measurements indicate the presence of an orthorhombic distortion. Plan view TEM analyses reveal two sets of misfit relieving dislocations at the interface. Dislocations are observed in films as thin as 14Å with an increase in density as the film becomes thicker. As the thickness of the films exceed 80Å, an orthogonal set of dislocations is observed which also increase in density as the thickness of the films is increased further. Films were studied with transmission electron microscopy (TEM) images at a variety of different thicknesses and compared to the RBS results of the same samples. Results will be presented which show that the 80Å films are fully relieved in the  $\langle 110 \rangle$  direction and almost fully strained in the  $\langle 100 \rangle$  direction. The RBS measurements will be shown to be entirely consistent with TEM results.

## ***APPENDIX***

### ***ADDRESS LIST OF INVITED SPEAKERS***

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